Energy, Mines and Resources Canada

Énergie, Mines et Ressources Canada

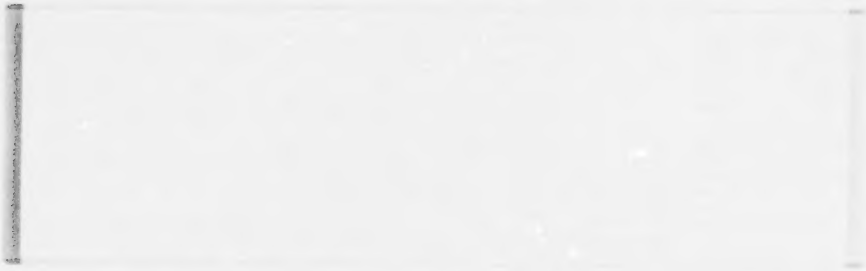
CANMET

Canada Centre for Mineral and Energy Technology

Centre canadien de la technologie des minéraux et de l'énergie

Metals Technology Laboratories

Laboratoires de la technologie des métaux



Canada

CORROSION INHIBITION IN SOUR MEDIA

V.S. SASTRI

MTL 88-78(TR)

MICROMEDIA

This document is an interim report prepared for [illegible] and represents the opinion of the [illegible] for Mineral and Energy Technology (CANMET)

...ment est un rapport ...révisé et rédigé ... tout fin de ... documentation ... représente nulle... ...sition définitive de ... du Centre canadien de la technologie des minéraux et de l'énergie (CANMET)

53M

METALS TECHNOLOGY LABORATORIES
REPORT: MTL 88-78(TR)

CORROSION INHIBITION IN SOUR MEDIA

by

V.S. Sastri

ABSTRACT

Corrosion inhibition mechanisms, hydrophobicity and effect of structure of inhibitors in corrosion inhibition in sour media are presented. Application of Hammett's equation, surface analysis and quantum chemical calculations in rationalizing the behaviour of inhibitors has been discussed. Methods used for quality control of oil field corrosion inhibitors have been discussed. The application of a hard and soft acid and base (HSAB) principle in the classification of corrosion inhibitors has been advanced.

LABORATOIRES DE LA TECHNOLOGIE DES MÉTAUX
RAPPORT: LTM 88-78(TR)

INHIBITION DE LA CORROSION DANS LES MILIEUX ACIDES

par

V.S. Sastri

RÉSUMÉ

Le rapport porte sur les mécanismes d'inhibition de la corrosion, l'hydrophobicité et l'effet de la structure des inhibiteurs sur l'inhibition de la corrosion dans les milieux acides. L'application de l'équation de Hammetts, le rôle de l'analyse de la surface et les calculs chimiques (théorie des quanta) pour rationaliser le comportement des inhibiteurs font l'objet d'une étude. Les méthodes utilisées pour le contrôle de la qualité des inhibiteurs de corrosion des champs pétrolifères sont également présentées. On a proposé l'utilisation d,un acide doux et d'un acide fortement concentré et l'application du principe de base (HSAB) pour la classification des inhibiteurs de corrosion.

I. INTRODUCTION

The role of corrosion inhibitors in primary production, secondary recovery, refinery product problems and storage and transportation of petroleum has been well documented (1-4). Corrosion inhibitors find wide and diverse application in the oil and gas industry, because of the exceptionally aggressive properties of the corrosive environments encountered and because of the technological and economic benefits gained from the use of inhibitors.

Oil and gas wells are either sweet or sour. Sweet wells do not contain hydrogen sulphide whereas sour wells do. The predominant corrosive agent in sweet wells is carbon dioxide. Sweet wells are further classified into flowing oil wells, gas-lift wells, pumping oil wells, and gas condensate wells. Corrosive acids such as formic and acetic acids may be present in sweet wells. On the other hand, in the case of sour wells, hydrogen sulphide is the primary corrosive agent, and frequently carbon dioxide is present as well. The corrosion caused by carbon dioxide and hydrogen sulphide and the inhibition of corrosion are discussed in the following section.

II. CARBON DIOXIDE CORROSION

Carbon dioxide as a rule increases the corrosion rate of steel which requires the presence of increased amounts of water as illustrated by the following data :

Water content of wells (%)	Corrosive wells (%)
0 - 20	0
20 - 40	0 - 30
40 - 60	50 - 100
60 - 100	100

The water produced with oil is generally a brine containing 1-10% sodium chloride and also contains considerable amounts of calcium, magnesium, barium, sulphate and other constituents generally present in sea water. The pH of this brine is affected by the presence of carbon dioxide and acetic acid and is generally acidic. Although the corrosive mechanism of carbon dioxide is not entirely clear, acidification of the medium from carbonic acid is generally considered to be a prime factor in causing corrosion. Acids such as acetic acid cause general corrosion; carbon dioxide can cause pitting attack. Other types of attack are "ringworm" corrosion and erosion corrosion. "Ringworm" corrosion can be either smooth or a deeply pitted type of attack. Corrosion caused by carbon dioxide depends upon the carbon dioxide partial pressure as

follows: partial pressure above 30 psi usually indicates corrosion; partial pressure between 7 and 30 psi may indicate corrosion; partial pressure below 7 psi is considered non-corrosive.

CORROSION RATES IN CARBON DIOXIDE SOLUTIONS

The uniform (general) corrosion rate of steel increases with increase in CO_2 concentration. Most of the early literature attributes this trend to increasing acidity caused by increasing CO_2 concentration -

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \overset{pK_1\ 6.37}{\rightleftharpoons} H^+ + HCO_3^- \overset{pK_2\ 10.33}{\rightleftharpoons} H^+ + CO_3^=$$

The pK_1 value of 6.37 is the apparent value and it suggests that the CO_2 containing solution would be slightly acidic. In actuality the true pK_1 value is around 5, and this would make the solution more acidic than the value based on the apparent pK_1 of 6.37. Although the decreased pH value is a significant factor, CO_2 has been shown to have a more direct role because corrosion rates in CO_2 containing solutions are higher than in solutions of highly dissociated (strong) acids of the same concentrations.

The uniform corrosion of iron proceeds by a coupled electro-chemical reaction. When no solid reaction products are formed the anodic dissolution reaction is

$$Fe \rightarrow Fe^{2+} + 2e^-$$

The above reaction proceeds through intermediates involving hydroxyl ions in such a way that its rate decreases with decreasing pH (5). This effect is seldom noted in corrosion practice because it is usually controlled by the cathodic reaction. In deaerated media the cathodic reaction is

$$2H^+ + 2e^- \rightarrow H_2$$

The increase in rate of the above cathodic reaction with decreasing pH more than offsets the pH dependence of the anodic reaction and the net effect is that corrosion rates increase with decreasing pH.

Carbon dioxide appears to affect the cathodic reaction primarily. deWaard and Milliams (6) proposed that hydrogen evolution occurs from carbonic acid as follows -

$$H_2CO_3 + e^- \rightarrow H + HCO_3^- \ ; \ H + H \rightarrow H_2$$

$$HCO_3^- + H^+ \rightarrow H_2CO_3$$

In a sense carbonic acid "catalyses" the hydrogen evolution reaction.

According to Schwenk (7) carbon dioxide augments mass transfer of hydrogen ions to the metal surface. Thus, hydrogen is evolved from hydrogen ions produced by the ionization of carbonic acid, near the surface rather than from carbonic acid directly. The high concentration of carbonic acid or its precursor CO_2 relative to the concentration of hydrogen ions in solution increases overall mass transfer rates and depolarizes the cathodic reaction. The distinction between this point of view and that of deWaard may seem rather small, but it could affect the dependence of corrosion rate on carbon dioxide concentration under certain conditions.

CORROSION INHIBITION IN ENVIRONMENTS CONTAINING CARBON DIOXIDE

Corrosion inhibitors used in combating corrosion in sweet wells include chromates, arsenic compounds, neutralizing compounds and organic nitrogenous compounds.

Chromates

The use of dichromates alone or in alkaline solutions for the prevention of corrosion in oil wells was known as far back as 1925 (8). Chromates are used as inhibitors in controlling corrosion in gas condensate wells. Thirteen parts per million of zinc chromate give steel adequate protection against corrosion in a medium containing 52,000 ppm of sodium chloride with a pH of 6.2. Zinc chromate was effective as a corrosion inhibitor at pH 3.0 even in the presence of oxygen (9).

In the case of gas condensate wells, 3000-6000 ppm of dichromate is used initially, followed by 200-400 ppm at later stages for adequate protection (1).

According to Hackerman and Hurd (10) corrosion inhibition of steel by dichromate involves the development of high pH in a liquid film adjacent to the metal followed by precipitation of a protective coating in solution which is acidic at other points. This film is thought to act as a mechanical barrier between the metal and its environment.

There are two drawbacks to using chromate as an inhibitor - (i) it can cause plugging by the formation of chromium oxide, (ii) chromate is toxic.

In order to elucidate the mechanism of corrosion inhibition by chromate it is necessary to subject steel surfaces to analysis by surface analytical techniques such as ESCA, Auger, SIMS and microprobe. It is also instructive to study and compare non-toxic analogues, such as molybdate and tungstate, for corrosion control.

NEUTRALIZATION INHIBITIONS

Alkaline inhibitors, such as ammonia, sodium hydroxide, sodium carbonate, sodium bicarbonate and sodium silicate have been used in gas condensate wells (1). The mechanism of corrosion inhibition with this class of inhibitors involves neutralization of the corrosive agents and formation of bicarbonates with carbon dioxide. The bicarbonate formed results in the medium being buffered at pH 8.4.

The main drawback of these inhibitors is that its application is limited to systems containing low solids, preferably below 2000 ppm and the total calcium and magnesium contents should be less than 300 ppm. Otherwise alkaline earth scales are formed, resulting in severe plugging problems.

ARSENIC COMPOUNDS

Use of an aqueous mixture of arsenious oxide and sodium hydroxide as an inhibitor in sweet wells is well-known (1). A combination of sodium arsenite and arsenious oxide has been used as a corrosion inhibitor. This formulation has the advantage that sodium arsenite dissolves rapidly and gives the desired high initial concentration whereas the oxide dissolves slowly and gives the low, long-term inhibitor level. Frisius (11) proposed a formulation consisting of boric acid, arsenious oxide and sodium hydroxide, which enlarges the pH range over which the formulation can be used safely without the precipitation of arsenious oxide due to the presence of CO_2 in the well fluids.

There is very little information in the literature on the mechanism of corrosion inhibition of arsenic compounds in oil well systems. However Bregman (1) suggests that the inhibition bears a strong relationship to the accepted protective mechanism of cathodic inhibition of steels in aqueous acid media. Bailey (12) postulates that the protective mechanism is from the formation of a compact thin film of elemental arsenic on the steel surface. As hydrogen atoms are formed they combine with arsenic to form arsine which is toxic. Since arsenic also prevents hydrogen atom recombination to form molecular hydrogen, hydrogen atoms build-up on the surface and suppress more hydrogen atom formation which leads to cathodic inhibition.

The chief drawback of using arsenates as inhibitors is the formation of arsine, which is poisonous.

ORGANIC INHIBITORS

The corrosion inhibitors currently used to combat carbon dioxide corrosion have been summarized in Table 1. In the majority of cases compounds such as monoethanolamine, triethanolamine and glycol-ethanolamine mixtures have been used for removal of carbon dioxide by an absorption process. Small amounts of salts of transition metals such as Cu, Cr, Co, V and Ni have been used along with alkanolamines, but no discussion of the role played by these salts has

been reported. From the chemistry of these transition metals it is possible to speculate that mixed amine carbonato complexes of the metals may be formed in solution, especially in the case of cobalt and copper salts which minimize corrosion.

Use of ammonium thiocyanate in combination with Co, Ni, Cr salts in corrosion control has been advanced without any mention of the mechanism. Thiocyanato complexes of these metals are probably involved in producing synergistic effects in corrosion inhibition. This is an area which requires more detailed study both from solution chemistry and surface analysis approaches.

Pyridine bases and quaternary ammonium salts such as dimethyl and trimethyl alkylammonium chlorides have been used to combat carbon dioxide corrosion and no mechanism of corrosion inhibition by these compounds has so far been advanced. By analogy with hydrogen sulphide corrosion it is possible to speculate that a species of the following type is formed which is stabilized by the quaternary ammonium salt

$$Fe \text{ --- } HCO_3^- \text{ --- } + N^+\text{-}R_4 \text{ (where R = alkyl group)}$$

To understand and propose a plausible corrosion inhibition mechanism requires that a variety of substituted quaternary ammonium salts used as corrosion inhibitors be studied, including surface analysis of the steel samples exposed to this medium.

III. HYDROGEN SULPHIDE CORROSION

The corrosion problem in oil wells containing hydrogen sulphide has been a serious one for many years (1). According to Stanton (13) one can encounter any of the following types of corrosive attacks in oil wells - electrochemical, sulphide stress corrosion cracking, erosion-corrosion, embrittlement, blistering, microbiological, galvanic and electrolytic. Hydrogen sulphide markedly increases the corrosion rate - for example the corrosion rate of mild steel increased from 10 mpy in synthetic oil well fluid to 60 mpy as the hydrogen sulphide content increased from 0-100%.

Before examining the hydrogen sulphide corrosion it is useful to record the percentage of various species of hydrogen sulphide present in solution as a function of pH (3).

pH	4	5	6	7	7.5	8	8.5	9	10
C_{H_2S}(%)	99.9	98.9	91.8	52.9	26	10.1	3.4	1.1	0.1
C_{HS^-}(%)	0.1	1.1	8.2	47.1	74	89.9	96.6	98.9	99.9
$C_{S^=}$(%)	---	---	---	---	--	---	---	0.01	0.1

The above data were obtained based on the values of the two dissociation constants of H_2S, K_1 and K_2 being 8.9×10^{-8} and 1.3×10^{-13} respectively. At pH 4 hydrogen sulphide is present almost entirely in the molecular form, and, above pH 6, bisulphide (hydrosulphide) concentration becomes appreciable. In many gas deposits, the H_2S content is about 5 to 10 mass per cent, and its concentration in water condensate is 250-500 ppm. In addition to H_2S, sour natural gas contains CO_2 which is responsible for the acid pH; hence, the major portion of the H_2S absorbed by the water or CO_2 condensate is in the molecular form. On this basis, the theories which propose that hydrogen sulphide corrosion is due to the catalytic role of bisulphide and sulphide ions are to be viewed with skepticism. On the other hand, iron sulphides have been detected among the corrosion products which can form only as a result of ionic reactions. The presence of various iron sulphides in the corrosion products at different concentrations of hydrogen sulphide have been identified. Based on this evidence the net corrosion reaction due to hydrogen sulphide can be written as:

$$Fe + H_2S \rightarrow FeS + 2H^+ + 2e^-$$

The above reaction responsible for hydrogen sulphide corrosion and hydrogen embrittlement is a very simplistic picture and does not present the true mechanism.

Many mechanisms for hydrogen sulphide corrosion have been presented in the literature. Makrides and Hackerman (14) proposed a catalytic mechanism consisting of the formation of an intermediate compound of iron and sulphur which is characterized by a lower energy of transfer across the phase boundary than that of iron ions. This intermediate compound decomposes in an acid medium and regenerates sulphide ions. Because sulphide ions form in the vicinity of the metal surface, even small amounts of H_2S accelerate the corrosion process.

In analogy with hydroxyl ions, Iofa (15) postulates the following scheme -

$$Fe + H_2S + H_2O \rightarrow FeHS_{ads}^- + H_3O^+$$
$$FeHS_{ads}^- \rightarrow (FeHS)^+ + 2e^-$$
$$(FeHS)^+ + H_3O^+ \rightarrow Fe^{2+} + H_2S + H_2O$$

Panasenko (16) put forward a scheme involving the adsorption of molecular H_2S on the metal -

$$Fe + H_2S \rightarrow Fe(H_2S)_{ads}$$
$$Fe(H_2S)_{ads} \rightarrow (Fe.H_2S)^{2+} + 2e^-$$
$$(Fe.H_2S)^{2+} \rightarrow Fe^{2+} + H_2S$$

The strong bond between the metal and H_2S apparently leads to the weakening of metal-metal bonds facilitating passage of metal into solution.

The cathodic reaction is also speeded up by the presence of hydrogen sulphide. Panasenko presents the following scheme:

$$(H_2S)_{ads} + H_3O^+ \rightarrow (H_3S^+)_{ads} + H_2O$$
$$(H_3S^+)_{ads} + e^- + M \rightarrow H - M - (H_2S)_{ads}$$
$$H_3O^+ + e^- + M \rightarrow H - M - H_2O$$

The above scheme has been criticized in view of the evidence for adsorption of bisulphide ion (HS^-) rather than molecular hydrogen sulphide.

Bolmer (17) is of the opinion that the reduction of the hydrogen over voltage in the presence of hydrogen sulphide is related to the ease of discharge of hydrogen from molecular hydrogen sulphide and advances the scheme -

$$2H_2S + 2e^- \rightarrow H_2 + 2HS^-$$
$$HS^- + H_3O^+ \rightarrow H_2S + H_2O$$

Kaesche (18) is of the opinion that the discharge of hydrogen ions from H_2S molecules is energetically more favourable than the discharge from hydronium ions, due to lower dissociation energy of H-SH bond than H-OH bond. Reduction of the H_2S molecule can proceed thus.

$$H_2S + 2e^- \rightarrow 2H_{ads} + S^{2-}$$

From the above schemes it is clear that hydrogen sulphide is regenerated and even trace amounts of the hydrogen sulphide greatly speed up the cathodic process. The limiting diffusion current observed in current - voltage scans increases with increase in partial pressure of H_2S and this observation led to the view that hydrogen ions are discharged from molecular hydrogen sulphide. But the limiting current observed with studies involving a rotating disc electrode was not influenced by the change in H_2S concentration and this shows that hydrogen sulphide is not directly involved in the cathodic process, and it may act as a catalyst in speeding up the discharge of hydrogen ions.

The most probable mechanism of the accelerating effect of hydrogen sulphide involves the formation of a molecular surface complex Fe(H-S-H)ads which on cathodic polarization yields hydrogen atoms. Some of the hydrogen atoms may recombine while others diffuse into the metal.

$$Fe + HS^- \rightarrow Fe(HS^-)_{ads}$$
$$Fe(HS^-)_{ads} + H_3O^+ \rightarrow Fe(H\text{-}S\text{-}H)_{ads} + H_2O$$
$$Fe(H\text{-}S\text{-}H)_{ads} + e^- \rightarrow Fe(HS^-)_{ads} + H_{ads}$$

According to LeBoucher the surface concentration and activity of the molecular complex Fe(H-S-H) depend upon the stability of the bond between iron atoms and the ions and the ease with which hydronium ions approach the electrode. If the electrode charge is negative, hydronium ions can approach the electrode to form the molecular complex. However, at negative potentials, HS^- adsorption weakens. The formation of the catalytic molecular surface complex predominates over the reduced adsorption of SH^-. Thus, the corrosive attack of H_2S can be eliminated by applying very high negative potentials when HS^- ions are desorbed and no catalytic molecular complex is formed. At very high positive potentials the adsorption of HS^- and the bond strength between Fe and HS^- is high but the labile molecular complex does not form and the catalytic effect is diminished.

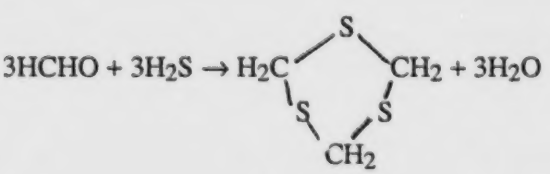
CORROSION INHIBITION IN ENVIRONMENTS CONTAINING HYDROGEN SULPHIDE

Corrosion inhibitors used in combating corrosion in sour wells include aldehydes, cyanamides and a host of other organic compounds.

Aldehydes

Formaldehyde was one of the earliest inhibitors used to control corrosion in a hydrogen sulphide medium (1). At present it is used only as an adjunct to other complex organic inhibitors. The amount of formaldehyde used depends upon the composition of the brine, the amount of hydrogen sulphide and the daily flow of the well. The average amount of formaldehyde used varies from 15 to 80 mg/L.

In acids, formaldehyde reacts with hydrogen sulphide forming trithioformaldehyde thus



The trithioformaldehyde (trithiane) formed protects the metal from corrosion.

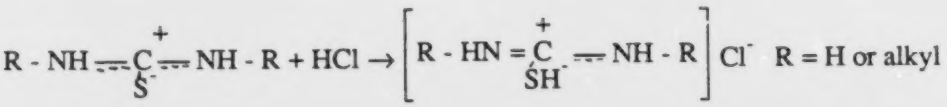
It has been shown that branched chain aldehydes such as isobutyraldehyde are more effective than straight chain aldehydes (butyraldehyde) as corrosion inhibitors.

Cyanamides

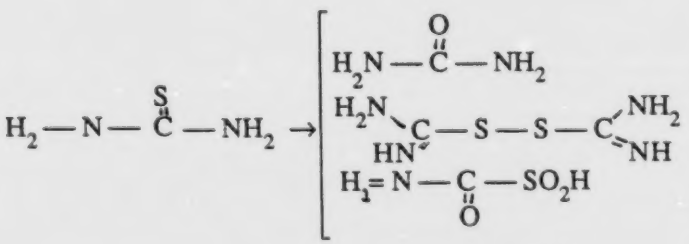
Menaul patented the use of cyanamides for corrosion inhibition in sour oil wells. Calcium, barium, magnesium, dimethyl, diethyl and diallyl cyanamides, and dicyanamides of calcium, barium and magnesium are typical of the compounds used. The inhibiting effect of cyanamides is thought to result from a film consisting of a bond between the nitrogen in cyanamide and iron. Surface analysis of the films formed using X-ray photo-electron spectroscopy (XPS), Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS) might elucidate further corrosion inhibition by cyanamides.

Thiourea and Urea Derivatives

Thiourea and its derivatives have been in use as corrosion inhibitors. In acidic solutions thiourea undergoes decomposition and hence both thiourea and its decomposition products may be detected on the metal surface. In an acidic solution the following equilibria exist in solution (19) -



Hydrolysis of thiourea produces hydrogen sulphide and carbon dioxide. Oxidation of thiourea forms urea, formamidine disulphide or sulphonic acid depending upon the reaction conditions.



These reactions are presented here so that one may be aware of the chemical species that exist under different conditions.

Corrosion inhibition by thiourea and its derivatives is more effective in the presence of hydrogen sulphide than in its absence. Saturation of acid solutions with hydrogen sulphide increased the corrosion inhibition by thiourea and the degree of protection increased with increasing concentration of thiourea. The effectiveness of thiourea as an inhibitor decreases with increasing temperatures. In the presence of hydrogen sulphide, thiourea shifts the corrosion

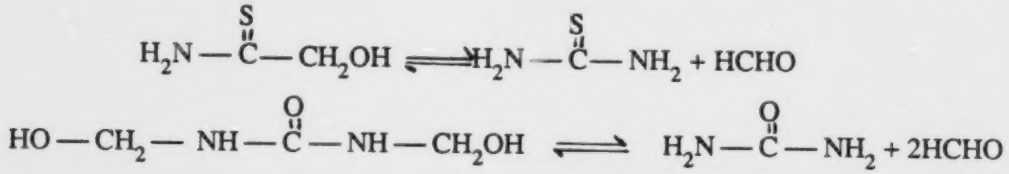
potential to more positive potentials, indicating that corrosion inhibition by thiourea is predominantly under anodic control.

In the presence of hydrogen sulphide, monomethylol thiourea (MMU) inhibits corrosion of steel, and the degree of inhibition increases with temperature. MMU inhibits corrosion in presence of hydrogen sulphide by about a factor of 20 to 50 at an inhibitor concentration of 1.0 g/L or more compared with the rate in the absence of hydrogen sulphide.

Studies on urea and dimethylol urea (DMU) showed them to be less effective corrosion inhibitors than thiourea and its derivatives. The effectiveness of urea as an inhibitor decreases sharply in the presence of hydrogen sulphide, and the decrease is more pronounced at higher temperatures. On the other hand DMU decreased the extent of corrosion of steel in the presence of hydrogen sulphide by a factor of 50 to 100 at concentrations greater than 0.1 g/L compared with the rate in the absence of hydrogen sulphide. At concentrations of 0.5 to 1.0 g/L and at temperatures of 50 to 90°C DMU functions more effectively than MMU and gives a protection up to 99.9%. Potentiodynamic polarization measurements confirm that both cathodic and anodic processes are retarded in the presence of DMU, confirming its effectiveness as a corrosion inhibitor.

MECHANISM OF INHIBITION BY THIOUREA AND UREA DERIVATIVES

The experimental data on the corrosion rates and polarization behaviour obtained with thiourea and urea derivatives as inhibitors in the presence of hydrogen sulphide showed similarity in behaviour, suggesting the possibility of a similar inhibition mechanism. Monomethylol thiourea (MMU) is synthesized by treating thiourea with formaldehyde (1:1 ratio) and dimethylol urea (DMU) is produced by the reaction of urea with 30-40% aqueous solution of formaldehyde in the ratio of 1:2 in an alkaline medium at 0 to 5°C. It is logical therefore that in acid solutions both MMU and DMU undergo decomposition producing formaldehyde as a product.



The formaldehyde produced as a product of the decomposition of the inhibitors MMU and DMU must be responsible for the corrosion inhibition, since formaldehyde can react with hydrogen sulphide producing trithioformaldehyde which gives a protective film on the surface of the metal. The presence of formaldehyde when DMU and MMU were used as corrosion inhibitors was detected by spectrophotometry, confirming the above hypothesis.

Phenylthiourea and diphenylthiourea were tested in an acid medium and no formaldehyde was detected, as expected. On the other hand urotropine (hexamethylenetetramine) which gave rise to formaldehyde as a product of decomposition was an effective corrosion inhibitor,

$$C_6H_{12}N_4 + 6H_2O + 4HCl \rightarrow 6HCHO + 4NH_4Cl$$

The formation of trithioformaldehyde by the reaction of formaldehyde and hydrogen sulphide when MMU, DMU and urotropine were used as inhibitors was confirmed by UV and infared spectroscopy.

ORGANIC AMINES

While organic amines are known to be less effective inhibitors in acid solution, inhibition by amines in the presence of hydrogen sulphide is greatly enhanced, as evidenced by the data given below (3):

		Protective Effect	
Inhibitor	C_{Inh}(mole/L)	1 N H_2SO_4	1 N H_2SO_4+H_2S(Sat.)
Allylamine	0.5	3.4	8.7
Diallylamine	0.1	3.0	10.4
Triallylamine	0.1	4.4	33.6
Tributylamine	0.05	2.6	29.2
Tetrabutylammonium Sulphate	0.0005	1.0	96.0

The data given above show that a synergistic effect manifests itself in the presence of hydrogen sulphide. Normally hydrogen sulphide promotes corrosion and hydrogen embrittlement, but hydrogen sulphide increases the corrosion inhibition efficiency of organic amines. The synergistic effect of hydrogen sulphide has been ascribed to the fact that bisulphide anions (HS^-) adsorbed on the iron act as anion bridges facilitating the adsorption of cation type inhibitor.

$$R\text{-}NH_2 + H^+ \rightarrow RNH_3^+$$

$$Fe\text{ -- }SH^- + RNH_3^+ \rightarrow Fe\text{ -- }SH^-\text{ -- }H_3\overset{+}{N}\text{ - }R$$

The surface compound Fe(H-S-R) is unable to supply protons for the cathodic process and also impedes anodic metal ionization reaction.

The inhibitors used for combating hydrogen sulphide attack on steels are presented in Table 2. Some typical compounds belonging to various classes are given below.

Phenols, substituted phenols, thio and bisthiobisphenols
Amines - tridecyl, pyridines, quinolines, imidazoline, poly(alkylene amine)
Polyamides - ethanolamines
Aminonitriles - diethylaminoacetonitrile
Aminoacetylenic alcohols
Quaternary salts - dodecyltrimethylammonium chloride, ethylammonium pyrocatechol borate, phosphonium compounds
Organic phosphites
Fatty acids - oleates
Acid hydrazides - Naphtenic acid hydrazide
Monoglyceride allyl ether.

Although a wide variety of compounds have been used as inhibitors in a hydrogen sulphide medium, only organic amines and quaternary ammonium salts find widespread application in the oil industry. There are many structural features of the amines and quaternay ammonium compounds which may contribute to the corrosion inhibition properties. Some of the structural factors of importance are the hydrophobicity of the inhibitor, electronic effects due to substituents on the inhibitor molecule and steric effects due to the bulky nature of the substituents in the inhibitor molecule. These aspects are discussed in the following paragraphs.

HYDROPHOBICITY OF INHIBITORS

Three classes of inhibitors, (i) imidazolines, (ii) imidazoles and (iii) fatty amines were studied (20) in deaerated medium containing 5 g/L of ammonium chloride saturated with hydrogen sulphide at a pH of 4.0. In the case of some imidazoline derivatives and aliphatic fatty amines, corrosion inhibition efficiency increased with increase in concentration of the inhibitor and finally reached a plateau. In the case of some substituted imidazole deriratives the inhibition efficiency increased very slightly at first followed by a significant increase and then reached a plateau, with increasing concentration of the inhibitor. The concentration at which a break in slope was observed agreed well with the critical aggregation concentration of the inhibitor. Inhibition by imidazoline derivatives increased at 35°C compared with room temperature and the temperature of 35°C corresponds to the Kraft temperature at which association of the inhibitor molecules takes place. In the case of substituted imidazolines the inhibition efficiency increases with increase in the

number of carbon atoms present in the hydrophobic chain and decreases beyond 10-14 carbon atoms in the chain.

These observations show that there is a relationship between the formation of aggregates in solution and changes in the inhibition efficiency of the compound studied. This can be attributed to structural changes in the adsorption layer. Using polarographic techniques, the effect of micellization on the structure of the electrical double layer and the adsorption potential of micelles has been documented.

The Hansch model was used (20) for providing a quantitative basis for the correlation of corrosion inhibition efficiencies with the hydrophobicity parameter. This is based on the assumption that the behaviour of the corrosion inhibitor is similar to the behaviour of a drug molecule with respect to the receptors of the host organism.

The inhibition efficiency (log 1/c) of the substituted amines [CH_3-$(CH_2)_n NH_2$] was calculated using the equation

$$\log (1/c) = a.f^2 + bf + c$$

where "f" is the hydrophobicity factor for amines with n ranging from 7 to 17. The resulting values are given below:

n	log (1/c)	c.m.c. at 25°C mole/L	f	$K_b \times 10^{-4}$
7	2.56	1.6×10^{-1}	3.01	4.5
9	3.80	3.06×10^{-2}	4.06	4.4
10	4.16	1.13×10^{-2}	4.59	4.3
11	4.88	8.95×10^{-3}	5.11	4.3
12	5.32	5.50×10^{-3}	5.64	4.3
13	5.18	4.40×10^{-3}	6.17	4.2
15	5.70	1.39×10^{-3}	7.22	4.1
17	5.0	0.44×10^{-3}	8.28	4.0

The data given above show that the progressive increase in corrosion inhibition efficiency parallels the increase in hydrophobicity of the substituted amines up to an "n" value of 14, and corrosion inhibition efficiency does not bear any relationship to the basicity of the amine. The inhibition efficiency and the hydrophobicity factor increase progressively, paralleling the decrease in critical micelle concentration.

Similar analysis for imidazoline deriratives using the equations:

$$\log i_{corr.} = af^2 + bf + c$$
$$\log i_{corr.} = af^2 + bf + c \log |p| + d$$

generated the data given below (20):

	log i_{corr}		c.m.c.		
	10^{-5} mL^{-1}	5 x 10^{-4} mL^{-1}	mL^{-1}	f	log | p |
$(CH_2)_7$	4.38	5.0	1.0 x 10^{-2}	4.39	1.10
$(CH_2)_{10}$	4.57	5.46	7.2 x 10^{-3}	5.97	1.16
$(CH_2)_{13}$	4.66	5.38	2.5 x 10^{-3}	7.55	1.19
$(CH_2)_{15}$	4.54	5.47	1.7 x 10^{-3}	8.60	1.21
$(CH_2)_{17}$	4.72	5.16	7.8 x 10^{-4}	9.66	1.26

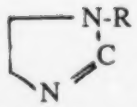
These data show that the corrosion currents vary with varying values of hydrophobicity factor. It is also shown that the equation involving both hydrophobicity (f) and polarity (p) parameters gives a better agreement than when hydrophobicity alone is taken into account. Corrosion inhibition efficiency increases to a maximum for a hydrophobic chain containing 10-14 carbon atoms, and then decreases when the number of carbon atoms increases beyond 14. This indicates that the transport of the active substance to the receptor plays an important role.

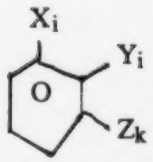
Furthermore, the improvement in correlation when both the polarity and hydrophobicity parameters are taken into account reveals the relationships existing between phenomena at the solid-liquid interfaces and micellization. These relationships involve a modification in the electrical double layer for concentrations in the vicinity of critical micelle concentrations. The results for imidazoline derivatives show better correlations at concentrations close to critical micelle concentrations than concentrations farther removed from critical micelle concentrations.

This approach is promising from both the theoretical and practical points of view since it opens up the possibility of rationally selecting an inhibitor and the importance of a knowledge of Kraft temperature and critical concentrations of the inhibitor compounds being used.

EFFECT OF INHIBITOR STRUCTURE ON CORROSION INHIBITION

Dupin and coworkers (21) studied the effect of structural changes on corrosion inhibition properties of a homologous series of imidazolines on steel in a deaerated medium containing hydrogen sulphide. The compounds studied had the general structure -





$R = H_1 - CH_2 - CH_2 - NH_2$

$X_i = H_1, CH_3$ Cl

$Z_k = H_1$ C_6H_5, $C(CH_3)_3$, CH_3NO_2, Cl

The measured corrosion current i is related to the substituents by the equation:

$$\log i_{corr.} = \gamma + e_i x_i + e_j Y_j + e_k Z_k$$

The contribution of different substituents or fragments is given below:

γ (skeleton)	2.6
$-(CH_2)-NH_2$	1.7
p.C_6H_5	0.57
-H	1.40
m.OCH_3	0.28
p.Cl	0.24
o.CH_3	0.16
o.Cl	0.13
p.t.Bu	0.08
p.CH_3	0.02
m.H	0.02
o.H	-0.07
p.H	-0.10
p.NO_2	-0.22
m.CH_3	-0.24

	log i_{corr}	
Compound	Experimental	Calculated
1.	3.97	3.87
2.	3.91	4.09
3.	3.92	3.99
4.	4.01	4.07
5.	4.10	4.21
6.	4.09	4.20
7.	4.86	4.87
8.	4.43	4.40
9.	4.48	4.55
10.	4.37	4.39
11.	4.48	4.43
12.	3.88	3.95
13.	4.20	4.17
14.	4.06	4.08
15.	4.44	4.46

Using the contribution of the various fragments the calculated corrosion currents are compared with the experimental corrosion currents and the agreement between the two values is quite good.

The above structure reactivity relationship in a homologous series of compounds allows one to predict the corrosion inhibiting properties of the substituted compounds and therefore the most effective inhibitors.

The corrosion inhibition by a variety of substituted pyridine compounds was studied (22) in a medium of pH 4.5 containing 3000 ppm of hydrogen sulphide at an inhibitor concentration of 5×10^{-3}M, and the following data were obtained:

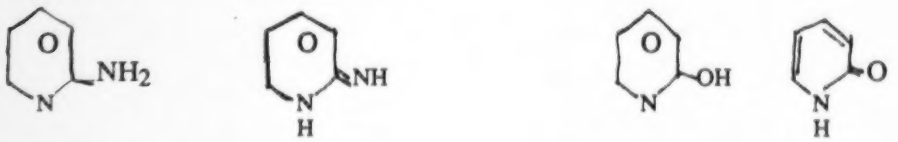
Substituent	Corr. rate	γ (protection)	σ_R	pKa
No inhibitor	1.284	---	---	---
Pyridine(H)	0.388	3.324	0	5.23
2-CH_3	0.304	4.224	-0.17	5.96
3-CH_3	0.308	4.169	-0.069	5.66
4-CH_3	0.216	5.944	-0.17	6.05
2,4$(CH_3)_2$	0.171	7.509	-0.34	6.63
2,5$(CH_3)_2$	0.194	6.618	-0.24	6.40
2,6$(CH_3)_2$	0.250	5.136	-0.34	6.75
3,5$(CH_3)_2$	0.278	4.618	-0.14	6.15
2,4,6,$(CH_3)_2$	0.210	6.109	-0.51	7.45
2-NH_2	0.139	9.237	-0.66	7.20
3-NH_2	0.233	5.511	-0.16	6.60
2-OH	0.444	2.832	-0.37	---
3-OH	0.337	3.810	0.13	4.86
2-Cl	0.501	2.570	0.21	0.72
3-Br	0.361	3.556	0.39	2.84
3,5$(Br)_2$	0.333	3.886	0.78	---
3-CN	0.375	3.424	0.56	1.45
3-COOH	0.378	3.397	0.34	2.07
3-$CONH_2$	0.362	3.547	0.28	---
4-$COOC_2H_5$	0.382	3.361	0.45	3.26

All the substituted pyridines affected the corrosion rates. The corrosion inhibition with compounds containing electron-donating substituents was found to be higher than with those containing electron-withdrawing substituents. For pyridines substituted in the 3 and 4 positions, plots of logaritham of corrosion protection coefficient (γ) vs σ_R substituent constant and the basicity (pKa) of the amine gave pairs of straight lines intersecting at a point corresponding to unsubstituted pyridine. When the electron density at the nitrogen atom is increased ($\sigma_R < O$) the protective capabilities of the pyridines increase sharply and when electron-withdrawing substituents are present ($\sigma_R > O$) the protection increases very slightly.

The presence of surface-active sulphide anions in the medium produces species like (Fe-SH), thereby reducing the positive charge on iron. Electrostatic adsorption on the iron by pyridines with decreased electron density (increase in σ_R values) is facilitated. Substituted pyridines with increased electron density on the nitrogen (negative values of σ_R) could bond to

iron directly (Fe---N). A similar trend was observed for the variation of corrosion rate with pK of the amines.

Deviations from the above trend have been observed in the case of 2 - chloro, 2 - hydroxy, - 2-amino-, and 2-methyl pyridines, 2,6-lutidine and 2,4,6 - collidine. The reduced protective properties of these compounds can be attributed to steric factors, and tautomerism [(2-aminopyridine) and (2-hydroxypyridine)].



Hammett's equation was used for correlation of corrosion rates with σ_R constants of the substituted pyridines:

$$\log K = \log K^\circ + \rho\sigma \; ; \; \log K = \log K^\circ + \beta(pKa - pK^\circ)$$

and the important conclusion is that the corrosion inhibition values of the substituted pyridines can be predicted by using these equations. It is also to be noted that those substituents (negative σ_R values) which increase the electron density at the nitrogen atom have the best corrosion inhibition properties.

Studies (23) on the corrosion inhibition of steel in 0.1 M HCl saturated with hydrogen sulphide by a variety of substituted arylamines did not give a close correlation of the inhibition efficiency with σ substituent constant given by Hammett's equation. Although the correlation of the inhibition efficiency with Hammett's substituent constant was not good, the arylamines proved to be quite effective in inhibiting the corrosion and hydrogen uptake by the steel. Introduction of a large nucleophilic substituent in the meta position of aryl amine increased the inhibition efficiency of the inhibitor. Cyclic alkyl substituent in the arylamine gave the best value for corrosion inhibition and in general the effect of the substituents has been attributed to steric factors.

The influence of the structure of pyridine derivatives with substituents of different polarity on the corrosion cracking of steel in solutions saturated with hydrogen sulphide at 30°C containing 5×10^{-3} mole of inhibitor at a stress of 980 MPa was studied recently (24). The protection coefficients of steel from corrosion cracking by inhibitors have been correlated to substituent constants σ and pKa of the amines by the equations -

$$\log K_p = \log K_p^\circ + \rho_p\sigma_R$$
$$\log K_p = \log K_p^\circ + \beta_p(pK_a - pK_a^\circ)$$

where K_p and K_p° are protection coefficients of substituted and unsubstituted pyridines, pK_a and pK_a° refer to substituted and unsubstituted pyridines, respectively. σ_R is Hammett's substituent parameter and ρ_p and $ß_p$ are proportionality constants. Plots of log K_p vs σ_r and log K_p vs pK_a gave a v-shaped curve with the break in slope occurring at a point corresponding to unsubstituted pyridine. The two lines with different slopes indicate the operation of two different mechanisms of adsorption of the pyridines on the steel. Nucleophilic substituted pyridines (negative values of σ_R) may be chemisorbed on the steel while electrophilic substituted pyridines are adsorbed in a physical sense. The line corresponding to positive values of σ_R is steeper than in the case of tests for general corrosion (larger angular coefficients). This is related to the fact that tensile stresses displace the charge of the surface of the metal in the negative direction. Hence substituted pyridines with positive values of σ_R (i.e. electrophilic substituents) are attracted to metal surface with ease and result in greater protection from corrosion cracking.

Although the mechanism of failure of steels in a hydrogen sulphide medium is not totally clear, it is generally assumed that sulphide cracking is caused by the penetration of hydrogen into the steel. The influence of substituents on the inhibitors in minimizing hydrogen entry into steel showed the validity of the following equations:

$$\log K_{H_2} = \log K_{H_2}^\circ + \rho_{H_2}\sigma_R$$
$$\log K_{H_2} = \log K_{H_2}^\circ + ß_{H_2}\,(pK_a - pK_a^\circ)$$

K_{H2} and K_{H2}° are the coefficients of retardation of hydrogen entry into the metal with substituted and unsubstituted pyridines, ρ_{H2} and $ß_{H2}$ are proportionality constants, characterizing the sensitivity of the degree of protection from hydrogen entry with derivatives of pyridine to the polarity of the substituents. σ_R is Hammett's substituent constant, pK_a and pK_a° are the basicities of substituted and unsubstituted pyridines, ρ_{H2} and $ß_{H2}$ are coefficients of proportionality, characterizing the sensitivity of the degree of protection of hydrogen entry with substituted pyridiners to the polarity of the substituents. The data show that both highly basic compounds (4-methyl-pyridine and 2,4,-dimethylpyridine) and less basic compounds (3-cyanopyridine and 3,5-dibromopyridine) offer effective protection from entry of hydrogen. Some of the substituted pyridines such as 2-hydroxy, 2-choloro, 2-amino, 2,6-dimethyl and 2,4,6-trimethylpyridines show deviations from the Hammett equation and this deviation is attributed to steric factors, aminoiminic and prototropic tautomerism which result in a weakening of metal-nitrogen bond.

The correlation coefficient, r, and the angular coefficients ρ and ß for both the nucleophilic and electrophilic substituted pyridines obtained by least squares method are given below:

Polarity (σ)	Test	ρ	rρ	ß	rß
$\sigma_R < 0$	Corrosion cracking	-2.79	0.97	0.334	0.89
	Hydrogen entry	-0.89	0.91	0.192	0.92
$\sigma_R > 0$	Corrosion cracking	1.49	0.99	-0.187	--
	Hydrogen entry	0.48	0.93	-0.058	0.90

Using the above values for the coefficients and the appropriate values of Hammett's σ_R values and the basicities of the substituted pyridines (pK) it is possible to predict the effectiveness of a substituted pyridine as an inhibitor for sulphide stress cracking and hydrogen impregnation of steel in a hydrogen sulphide medium.

Schmitt et al. (25,26) studied the influence of a variety of substituted quaternary ammonium salts on the uptake of hydrogen by unalloyed steel in H_2S-free and H_2S-saturated hydrochloric acid and H_2S-saturated formic acid solutions. Among the substituted pyridines the lowest hydrogen permeation rates were obtained with m-benzypyridine and 2,6-diphenylpyridine. This observation was attributed to both electronic and steric effects. Among the various substituted trialkylbenzylammonium chlorides tri-n-hexylbenzylammonium chloride and hexamethylenetetraminebenzyl chloride gave the lowest hydrogen permeation rates. This trend was attributed to steric effects, and the hydrophobic nature of the alkyl substituents on the nitrogen centre. The influence of benzylammonium chlorides (quaternary nitrogen atom is part of an aromatic system) on the hydrogen permeation rates showed the importance of steric, hydrophobic and electrostatic repulsion factors. In this family of compounds the best inhibitor was benzylquinolinium derivative. Substituents such as methyl, trifluoromethyl and methoxy groups on the benzyl phenyl ring in the quinolinium compounds exhibited adverse effects on the inhibition of hydrogen permeation rates.

No correlation could be found between Hammett's substituent parameter, σ, and the inhibition of hydrogen permeation in the case of substituted benzylquinolinium compounds. This eventuality is likely due to the expectation that the transmission of electronic density through the benzyl group would not be as efficient as it is through a phenyl group.

The counter ion associated with the benzylquinolinium and tri-n-butylbenzylammonium ions had a significant effect on the hydrogen permeation of the steel samples.

The order of inhibition of hydrogen uptake in the two sets of compounds in HCl and formic acid medium was as follows:

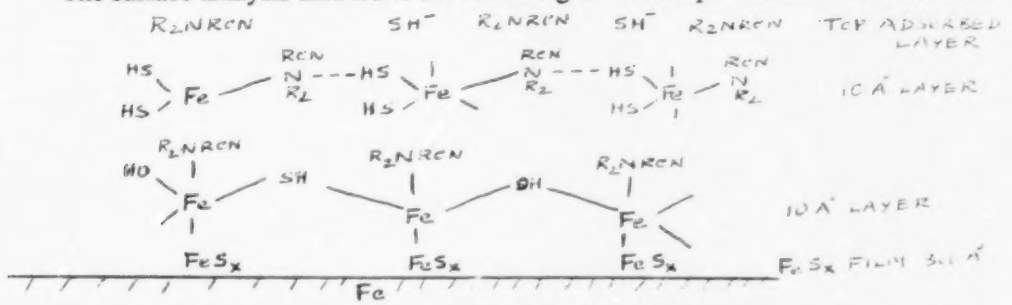
System	HCl	HCOOH
Benzylquinolinium	Cl > I ≈ Br	I > Br > Cl
Tri-n-butylbenzyl ammonium	Br > Cl ≈ I	Br > Cl ≈ I

The order of the inhibition in the case of tri-n-butyl benzyl ammonium ion is the same in both hydrochloric and formic acids (Br > Cl ≈ I) while it is different in the case of benzylquinolinium compounds. These differences cannot be easily explained on the basis of the known chemistry of these compounds. When the actual corrosion and the corrosion inhibition mechanisms in H_2S medium are better known, it may be possible to advance a rational explanation for the observed effects due to the presence of the various counter ions in the system.

SURFACE ANALYSIS OF SULPHIDE FILMS

Rozenfeld et al. (27) studied the nature of films formed on Armco iron in 0.5% NaCl, 250 ppm of acetic acid saturated with hydrogen sulphide by electron diffraction, Auger electron spectroscopy, XPS and secondary ion mass spectroscopy (Ion Microscopy). Auger spectral data showed the presence of protective layer 300 Å thick consisting of Fe, S, C and O. The following observations were made in the XPS spectra. Fe 2 $P_{3/2}$ peak shifted to lower binding energy indicating reduced charge on Fe atom. The unresolved doublet peak of N_{1s} showed two types of nitrogen - (i) Fe---N and (ii) C=N. The peak due to N_{1s} shifted to higher energy showing the donation of the lone pair of electrons on nitrogen to iron. The peak due to 2 P of sulphur showed the presence of SH- groups. Electron diffraction data showed the presence of Fe-S (makkinavite) on the iron metal. Ion microscopy gave peaks due to 15 (NH^+), 70 (FeN^+), 43($COHN^-$), 14 (N^+), 27 (CNH^+) and 71 ($FeNH^+$).

The surface analysis data led to the following schematic picture of the iron surface.


Fe
Fe
Fe

components in the inhibitor. Thus the quality control of the inhibitors used is an important aspect of maintaining performance level. Quality control checks, such as the measurement of viscosity, pour point and density, have been used in the past, but these checks do not provide an unambiguous estimate of the amount and nature of the active ingredient in the inhibitor formulation.

Recently, Martin et al. (28) applied spectroscopic techniques consisting of ^{13}C nuclear magnetic resonance (NMR) and Fourier transform-infrared spectroscopy (FT-IR) for quality control checks on corrosion inhibitors used in oil field systems. The most commonly used inhibitor formulation consisting of imidazoline, polymerized carboxylic acid, ethoxylated alcohol (surfactant) and an aromatic solvent, was investigated by the ^{13}C NMR and FT-IR techniques. The ^{13}C NMR peak assignment data are given below:

	Acid	Amide	Ester	Imidazoline	Alkene aromatic	Ethoxy	Alkane
Polymeric acid	179.8	----	173.4	----	130	----	14.4
Imidazoline (commercial)	----	173.5 173.3	----	167.7 167.2	126-135	----	14.53
Purified Imidazoline	----	----	----	167.9 167.6	126-135	----	14.53
Commercial Amide	----	173.9 173.7	----	----	126-135	----	14.53
Ethoxylated alcohol	----	----	----	----	70.4	----	14.32
Aromatic Solvent	----	----	----	----	120-145	---	14.40

The FT-IR peak data for the formulated inhibitor and its individual chemical components in the region 1800-1600 cm-1 are given below (28):

Component	Frequency (cm^{-1})
Polymeric acid	1730 (small shoulder) 1710
Commercial Imidazoline	1655 1610 1550
Ethoxylated alcohol	----
Aromatic solvent	1630 (weak) 1605 1510
Formulated Inhibitor	1730 1710 (shoulder) 1670 (small shoulder) 1655 1605 1550 1510
Inhibitor without solvent	1730 1710 (weak) 1670 (small shoulder) 1655 1550

The ^{13}C NMR and FT-IR peak position data help to identify the chemical components in the inhibitor qualitatively. Quantitative data on the amounts of various components were obtained from the plots of ^{13}C NMR peak height ratios of amine to ester and surfactant to ester versus the corresponding weight ratios.

Although ^{13}C NMR and FT-IR techniques have proven to be useful in laboratory quality control monitoring of corrosion inhibitions it is doubtful whether it would be sufficiently convenient and economical to use these techniques in actual field conditions because of the sophisticated and complex nature of these techniques, as well as the high cost of instrumentation . Thus there is an acute need for the development of simpler techniques for monitoring quality control of oil field corrosion inhibitors. Some of the promising techniques, such as gas chromatography, should be explored for monitoring the levels of the chemical components of the formulated inhibitors. Another technique that might prove useful in quality control of inhibitors is high pressure liquid chromatography (HPLC).

V. HARD AND SOFT ACID BASE (HSAB) CONCEPT IN CORROSION INHIBITION

Pearson (29) introduced the hard and soft acid and base concept in rationalizing the various chemical reactions in solution. Some of the characteristics of the hard and soft acids and bases are given below:

	Hard Acids	Soft Acids
Size	Small	Large
Electronegativity	High	Low
Polarizability	Low	High
Positive charge	High	Low
	Hard bases	Soft bases
Electronegativity	High	Low
Polarizability	Low	High
Ease of oxidation	Hard	Easy

Corrosion inhibitors can be viewed from the point of view of the HSAB principle and described as either hard or soft inhibitors. Inhibitors containing the following groups can be classified into hard, soft or borderline inhibitors:

Hard inhibitor	Soft inhibitor	Borderline inhibitor
H_2O, OH^-, F^- PO_4^{3-}	RSH, RS^- R_3P	$C_6H_5NH_2$, C_5H_5N, Br^-

Metal atoms, metal ions and bulk metals are classified as follows:

Hard Acids	Soft Acids	Borderline Acids
Fe^{3+}, Cr^{3+}, $MoO^{3+}Al^{3+}$	Cu^+,M°(metal atoms) bulk metals	Fe^{2+},Ni^{2+},Cu^{2+},Zn^{++}

In accordance with the rules of the HSAB principle, hard acids tend to form complexes with hard bases, and soft acids form complexes with soft bases. Borderline acids form complexes with either soft or hard bases.

Using the HSAB principle, one can rationalize the corrosion inhibition of iron and aluminum by phosphate in which iron phosphate and aluminum phosphate are produced. Ferric and Al^{3+} are hard acids, and they react with phosphate, a hard inhibitor and give corrosion

protection. Corrosion inhibition of Cu and Zn by amines can be rationalized by the formation of amine complexes of Cu^{2+} and Zn^{2+}, and this is in accord with the principle that Cu^{2+} and Zn^{2+} are borderline acids reacting with amines which belong to borderline inhibitors. Corrosion protection of copper (soft acid) by mercaptobenzothiazole (soft inhibitor) is also in keeping with HSAB principle.

As pointed out in Section III, the formation of iron sulphide, followed by Fe-SH species and bonding of iron to the nitrogen atom is encountered in sour media. The formation of these aforementioned species is in keeping with the HSAB principle because Fe atoms (soft acid) form compounds with SH^- (soft base).

It is important to point out that researchers may find it useful to apply HSAB principle more extensively in the design and selection of inhibitors in environments of interest.

VI. QUANTUM CHEMICAL STUDIES ON CORROSION INHIBITORS

Organic corrosion inhibitors are usually chosen for use in an environment of interest from empirical considerations based on macroscopic physico-chemical properties. Recently some work (31-33) on the theoretical prediction of the corrosion inhibition efficiencies of some organic inhibitors based on quantum chemical calculations has been done. Although quantum chemical calculations tend to be complex in the case of large organic molecules, these calculations can provide useful qualitative and semiquantitative information which may be used in the proper design and selection of corrosion inhibitors. Chakrabarti (31) used the simple Hückel molecular orbital theory in studying corrosion inhibition of mild steel in 6% HCl by biguanide, dicyanodiamide, guanyl urea and biuret compounds. A logarithmic plot of corrosion inhibition efficiency of the inhibitors showed a linear relationship with the highest occupied molecular orbital (HOMO) energy as well as with lowest unoccupied molecular orbital (LUMO) energy. The inhibitors, found to act as electron donors to the iron atoms, block the corrosion reaction by the formation of a bond (31).

The linear combination of atomic orbitals (LCAO)-self-consistent field (SCF) molecular orbital (MO) semiempirical method was used to study (32) linear chain diols, diamines and aliphatic aminoalcohols. The HOMO energies obtained were correlated with the inhibition efficiency of the inhibitors. Some typical data are given below (32):

	$H_2N(CH_2)_nNH_2$		
n	E(ev)	Geometry	Inhibition (%)
2	-9.094	Planar	84
3	-8.815	Planar	56.5
4	-9.197	Non-planar	-42

The data show that the corrosion inhibition is high when the molecule is planar and has a high energy value for HOMO.

Costa et al. (33) extended the use of the LCAO-SCF-MO method to the study of some nitrophenols and nitroanilines used in corrosion inhibition of titanium. Unlike the previous studies, this study included the metal atoms in the calculation and the formation of stable metal complexes. Typical data are given below (33):

Compound	Corrosion rate (mpy)	Stabilization energy (eV)
Phenol	88.6	1.77
O-Nitrophenol	1.8	4.40
M-Nitrophenol	0.2	4.44
P-Nitrophenol	0.3	4.50
Aniline	86.8	1.11
O-Nitroaniline	-	4.59
M-Nitroaniline	0.4	4.53
P-Nitroaniline	0.5	4.57

The correlations of the corrosion rate with the calculated stabilization energy is quite good considering the approximations used in the method of calculation.

A systematic study of the various substituted organic corrosion inhibitors used in sour media involving quantum chemical calculations using the LCAO-SCF-MO method and correlation of the stabilization energies with the corrosion inhibition efficiencies, is certainly warranted. This type of study would prove valuable in the design and selection of improved corrosion inhibitors.

REFERENCES

1. J.I. Bregman, "Corrosion Inhibitors", The Macmillan Co., New York, 1963.

2. C.N. Nathan, ed., "Corrosion Inhibitors", NACE Publication, Houston, Texas, 1973.

3. I.L. Rozenfeld, "Corrosion Inhibitors", McGraw-Hill Inc., New York, 1981.

4. L.E. Newton, Jr. and R.H. Hausler, "Carbon Dioxide Corrosion in Oil and Gas Production", NACE Publication, 1984.

5. F. Hilbert, Y. Mizoshi, G. Eichorn and W.J. Lorenz, J Electrochem.Soc, 118, 1919 (1971).

6. C. deWaard and D.E. Milliams, Corrosion, 31, 177 (1975).

7. W. Schwenk, Werkst. Korros., 25, 643 (1974).

8. J.C. Walker, U.S. Patent, 1,873,084, August 23, 1932.

9. R.E. Fariss, U.S. Patent, 2,695,876, Nov. 30, 1954.

10. N. Hackerman and R.M. Hurd, J. Electrochem. Soc., 98, 51 (1951).

11. E.N. Frisius, U.S. Patent, 2,885,359, May 5, 1959.

12. K.C. Bailey, quoted in "Metallic Corrosion Inhibitors", I.N. Putilova, S.A. Balezin and V.P. Barannic, Pergamon Press, New York, 1960.

13. J.P. Stanton, "A New Guide to Corrosion Control in Oil and Gas Wells", NACE T1a Meeting, Los Angeles, California, July 1959.

14. A.C. Makrides and N. Hackerman, Ind. Eng. Chem., 47, 1773 (1955); 46, 523 (1954).

15. Z.A. Iofa, Zachita Metallov, 6, 491 (1970).

16. V.F. Panasenko, Candidate's Dissertation, Polytekh. Inst., Kiev, 1972.

17. P. Bolmer, Corrosion, 21, 69 (1965).

18. H. Kaesche, Werkstoffe und Korrosion, 21, 185 (1970).

19. L.I. Antropov and V.F. Panasenko, Itogi Nauk i Tekhniki: Korroziya i Zashchita ot Korrozii, 4, 46 (1975).

20. P. Dupin, A. de Savignac and A. Lattes, Information Chimie, No. 228/229, 169 (1982).

21. P. Dupin, A. de Savignac and A. Lattes, Werkstoffe und Korrosion, 33, 203 (1982).

22. V.M. Zhovnirchuk, Yu. G. Skrypnik, Yu. I. Babei, S.N. Baranov and A.K. Mindyuk, Zashch. Met., 18, 638 (1982).

23. V.G. Starchak, L.D. Kosukhina, A.V. Manyachenko and V.M. Lebed, Zashch. Met., 20, 452 (1984).

24. V.M. Zhovnirchuk and Yu. I. Babei, Fiz.-Khim.Mekh.Mater, 19, 35 (1983).

25. G. Schmitt, B. Olbertz and K.R. Kurtz, Werkstoffe und Korrosion, 35, 107 (1984).

26. G. Schmitt and B. Olbertz, Werkstoffe und Korrosion, 35, 99 (1984).

27. I.L. Rozenfeld, d.B. Bogomolov, A.E. Gorodetskii, L.P. Kazanskii, L.V. Frolova and L.I. Shamova, Zashchita Metallov, 18, 163 (1982).

28. J.A. Martin and F.W. Valone, Corrosion, 41, 465 (1985).

29. R.G. Pearson, J. Chem. Education, 45, 581, 643 (1968); 64, 561 (1987).

30. J.Vesta and J. Eliasak, Corrosion Science, 11, 223 (1971)

31. A. Chakrabarti, British Corrosion Journal, 19, 124 (1984).

32. J.M. Costa and J.M. Lluch, Corrosion Science, 24, 929 (1984).

33. R. Sayós, M. González and J.M. Costa, Corrosion Science, 26, 927 (1986).

CARBON DIOXIDE MEDIUM (Sweet Wells):

1. Surface analysis of steel samples exposed to chromate inhibitor. Also investigate molybdate and tungstate as inhibitors in place of chromate along with surface analysis.

2. Surface analysis of samples exposed to arsenate inhibitor.

3. Study the use of Cobaltons chloride along with ammonia as an inhibitor and the possible formation of carbonate amine complexes of cobalt (III).

4. Ethanolamine and ammonium thiocyanate along with Co, Ni, Cr have been used as inhibitors. This system should be studied in detail and the possible formation of carbonato ethanolamine and thiocyanato complexes of metal ions should be identified.

5. Use of amines which form quarternary ammonium salts and hence act as corrosion inhibitors should be studied to see if there are similarities in the behaviour between CO_2 corrosion and H_2S corrosion.

HYDROGEN SULPHIDE MEDIUM (Sour Wells):

1. Surface analysis studies on samples exposed to inhibitors such as aldehydes and cyanamides should unravel the mechanism of inhibition.

2. Ion microscopic (SIMS) studies of samples exposed to amine inhibitors.

3. Explore the possible relationship between $(E - E_0)(\Delta E)$ - shift in potential with σ (Hammett substituent constant), binding energy shifts in XPS and PK's of a variety of substituted amines (e.g., pyridine).

4. Characterization oil field corrosion inhibitors by gas chromatograph/mass spectrometry and high pressure liquid chromatography.

5. Advance the concept of hard and soft inhibitors following hard and soft acid, base concepts.

6. Quantum chemical interpretation of the action of corrosion inhibitors.

APPENDIX 1 - CORROSION INHIBITOR DATA FOR CARBON DIOXIDE ENVIRONMENT

MATERIAL	MEDIUM	INHIBITOR	REFERENCE
Stainless steel 304	CO_2	Monoethanolamine saturated with CO_2 and 20 ppm of bismuth (III) citrate - 97% inhibition	1
AISI 304, Monel 400, AISI 1020	CO_2	Alkanolamines with thionitrogen compound 18-25% monoethanolamine with 200 ppm of NH_4 SCN giving 90-99% inhibition. Salts of Co, Ni, Ca, Cu, Cr, Zn, Sn, Al and Mg had synergistic effect	2
Carbon steel, AISI 304	CO_2	Triethomolamine (61 vol %) + 0.1 wt % $NaVO_3$ gave low corrosion	3
Steel (?)	CO_2	Cortron 2207 [78690-21-8]	4
Stainless steel [12597-58-1]	CO_2	K_2CO_3 solution containing 0.25% copper carbonate and antimonyl potassium tartrate, >99% inhibition	5
Stainless steel [12597-58-1]	CO_2	K_2CO_3 solution containing 0.5% $Fe_2(SO_4)_3$, 0.6%EDTA, 0.25% antimonyl potassium tartrate, >99% inhibition	6
Steel st 3 [39296-41-8]	CO_2	Monoethanolamine + >0.3 g of $Na_2Cr_2O_7$	7
Steel (?)	CO_2	Na_2SiO_3 - 0.5-0.65% + $K_2Cr_2O_7$ - 0.1-0.3%	8
Steel [12597-69-2]	CO_2	0.2% sodium metavanadate - >99% inhibition 0.33% vanadyl sulphate - 33% inhibition 0.2% potassium antimonyl tartrate + 0.02% tartaric acid - 67% 0.1% sodium metavanadate + 0.1% potassium antimonyl tartrate + 0.01% tartaric acid - >99%	9
Steel	CO_2 (7 kg/cm^2)	Pyridine bases	10
Carbon steel, stainless steel OKh22N5T (Cr-Ni-Ti), OKh21N6M2 (Cr,Ni,Mo) Kh17N13M2T (Cr,Ni,Mo,Ti)	CO_2	Glycol-ethanolamine 0.1% sodium vanadate or 0.5-1.0% Na_3PO_4	11
Carbon steel	CO_2 pH 12.4, 40% K_2CO_3	1.5-5.0% $NaNO_2$	12

MATERIAL	MEDIUM	INHIBITOR	REFERENCE
Carbon steel, st 45	CO_2	Dimethylalkylammonium chloride, Trimethylalkylammonium chloride, 1-B, 1 KB-4, Katapin A, 1 KB-4 (200 mg/L) - 85% inhibition Katapin A (100 mg/L) - 84% inhibition	13
Steel	CO_2 (50-110°C) 12-25% monoethanolamine	0.01% copper anthranilate	14
Carbon and stainless steels	CO_2 - monoethanolamine	Amine Guard (?)	15,16
St 3 sp, 16 GS, stainless OSKh22N6T, 12Kh18N10T	CO_2 - K_2CO_3	7% $Na_2B_4O_7$, $K_2Cr_2O_7$, V_2O_5, Bi_2O_3, Na_2SiO_3 (0.1% V_2O_5 + 0.7% $K_2Cr_2O_7$) 0.2-0.35 kg/h gave 96% inhibition	17
AISI 1020, AISI 304, AISI 33116, Monel alloy	30% monoethanolamine saturated with CO_2 at 250°C	NH_4SCN (200 ppm), NISO4 (50 ppm), Bismuth citrate (1 ppm) 1020 - 92%; 304 - 96%; 316 - 75%	18
AISI1020 steel	30% monoethylamine containing 0.30 mole CO_2	NH_4VO_3 (200 ppm V) + Fe^{2+} (50-250 ppm) gave corrosion <1 mil/yr COO2+ (30 ppm) + 200-400 ppm V gave <1 mil/yr	19

REFERENCES (Appendix 1)

1. B.D. Oakes, M.S. Dupart and D.C. Cringle; U.S. Patent US 4,420,337, 13th Dec. 1983; C.A., 100, 72357C (1984).

2. L.S. Krawczyk, C.W. Martin and R.L. Pearce, U.S. Patent US 4,431,563, 14th Feb. 1984; C.A., 100, 143324C (1984).

3. S.R. Mircetic, S.V. Stojanovic and C.Z. Kostic, Met Corros, Proc Int Congr Met. Corros/8th, 2, 1257 (1981); C.A. 97, 1113889t (1982).

4. L.N. Halstead, U.S. Patent 4,266,607, 12th May 1981; C.A. 95, 100008p (1981).

5. M. Okubo and K. Nagai, Japanese Patent, 7853,540, 16th May 1978; C.A. 89, 184106f (1978).

6. M. Okubo and K. Nagi, Japanese Patent, 7853,539, 16th May 1978; C.A. 89, 184107g (1978).

7. E. Rohumogi and M.B. Ferber, Tr. T Politekh. Inst., 359, 75 (1974); C.A. 86, 3255b (1977).

8. V.P. Khvatkova, M.S. Shchedrov and A.K. Nafikova, USSR Patent 489,522, 30th Oct. 1975; C.A., 84, 92176x (1976).

9. B.F. Mago, Ger Offen 2,518,827, 30th Oct. 1975; C.A.84, 51471z (1976).

10. Z.P. Obukhova and A.A. Kutovaya, Korroz. Zashch. Neftegazov. Prom-Sti, (5), 6 (1975); C.A., 83, 149909z (1975).

11. L.P. Barkar, I.K. Burtseva and J.A. Levin, Tr. Gos. Nauch.-Issled. Proekt. Inst. Azotn. Prom. Prod. Org. Siv, No. 14, 195 (1972); C.A., 80, 111459C (1974).

12. Z.A. Foroulis and B.E. Hopkinson, Ger. Offen. 2,135,343, 20th Jan. 1972; C.A., 76, 89211j (1972).

13. A.I. Obodov, Sb. Aspir. Rab., Ufim, Neft. Nauch.-Issled. Inst. No. 2,158 (1969); C.A., 75, 29208h (1971).

14. G. Balica and M.N. Neagoe, Rom. 41,079, 5th June 1968; C.A., 70, 31158g (1969).

15. K.F. Butwell and D.J. Kubek, Hydrocarbon Process, 56, 173 (1977); C.A., 88,, 140178f (1978).

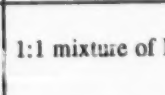
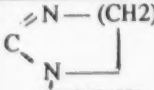
16. K.F. Butwell, E.N. Hawkes and B.F. Mago, Chem Eng Prog, 69, 57 (1973).

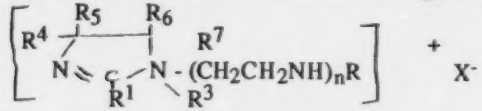
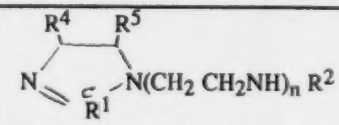
17. A.K. Nikitina, V.P. Khvatkova, V.M. Umnyashkina and L.P. Vershinina, Khim. Tekhnol. Topl. Masel., (8), 13 (1984); C.A., 101, 175550k (1984).

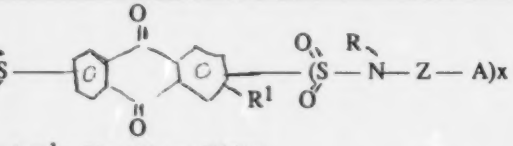
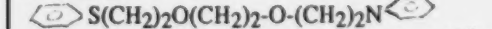
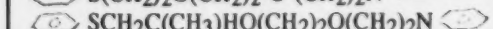
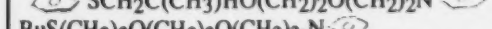
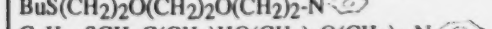
18. M.S. Dupart, B.D. Oakes and D.C. Cringle, U.S. Patent 4,446,119, 1st May 1984, C.A., 101, 27037h (1984).

19. E.C.Y. Nieh, U.S. Patent 4,372,873, 8th Feb. 1982; C.A. 98, 147779t (1983).

APPENDIX 2 - CORROSION INHIBITOR DATA FOR HYDROGEN SULPHIDE ENVIRONMENT

MATERIAL	MEDIUM	INHIBITOR	REFERENCE
Steel st 3 [39296-41-8]	H_2S - condensates of natural gas wells	Phenol, p-t butyl phenol, p-t amylphenol thio and dithiobisphenols	1
Steel (?)	(H_2S + CO_2) + 3% NaCl 50 wt % gasoline at 80°C	100 ppm N-tridecylmaleamic acid tridecylamine salt - 85% inhibition	2
Steel (?)	H_2S saturated acidified kerosine at 180°C	Synthesized from (a) poly (alkyleneamine) $NH_2R(NHR)_xNH_2$, R = C_2 - C_6 alkene, x = 0-12; (b) long chain fatty acid, (c) carboxylic acid, $CR_1R_2R_3COOH$ (R_1, R_2, R_3 - alkyls of C_3-C_2O) 5 ppm gave 33% inhibition	3
Steel (?)	Aqueous H_2S	2-Hydroxy-3-(dimethylaminomethyl)-5-tert.-butylphenyl nonyl sulphide	4
Steel (?)	H_2S, CO_2 in water-oil emulsions	1:1 mixture of  (CH2)n (n = 2, 3; x - OH/HN_2, R = n - $C_{17}H_{33}$ or iso - C_8H_{17}) and RC(=0) NH(CH2)n x (RCO can be tallow acyl) optimum level 250 ppm	5
Ferrous alloys	H_2S in highly mineralized medium	Ethylammonium pyrocatechol borate	6
Carbon steel	0.5% NaCl + acetic acid (pH 3.6) saturated to 1.7 g H_2S/L	General formula $R^2[NR^1)Z\ CN]_n$ (n = 1 or 2, z = C_{1-6} alkanediyl Diethylamino acetonitrite - 1 g/L gave >99% inhibition	7
Iron sheet	3% NaCl, 50% gasoline saturated with H_2S and CO_2 at 80°C	 (n = 1 or 2; R = C_{7-25} alkyl or akenyl) CH2(CH2)n NHCOR mixed with sulphur - 250 ppm gave 75% inhibition	8a, 8b
Ferrous metals	Alkanolamine containing sour gas	N(aminoethyl) ethanolamine/ethylenediamine, Propylenediamine/piperazine-N-(aminoethyl), Piperazine/methyliminebis(propylamine) containing V in 4^+ or 5^+ state	9
Steel SUS 316 L (stainless)	Aqueous H_2SO_4/$(HN_4)2$ SO_4/H_2S	Quinoline, pyridine bases isoquinoline, methylquinoline	10

MATERIAL	MEDIUM	INHIBITOR	REFERENCE
Sheet iron (?)	CO_2, H_2S water-oil emulsions (3% NaCl)	1-(2-aminoethyl)-2-isooctyl-2-imidazoline reacted with 5% sulphur at 150°C for 2 h. The product (250 ppm) gave 70% inhibition	11
Sheet iron (?)	50:50 emulsion of mineral spirits (3% NaCl) + CO_2 + H_2S	1-(2-oleamidoethyl)-2-imidazoline (250 ppm + 10% sulphur gave 83% inhibition - without sulphur gave 77% inhibition	12
Steel st 3 [39296-41-8]	5% NaCl + petroleum + H_2S	1-monoglyceride-3 allylether. Increase in chain length C_5-C_{12} gave increased inhibition	13
Steel (?)	H_2S, CO_2, 0.5% NaCl, pH 3.6 (acetic acid)	(Diethylamino) acetonitrite. 0.05 g/L - corrosion rate 0.2 mm/year 0.005 g/L - corrosion rate 7.22 mm/year	14
Steel SPY-3 L	5% NaCl + 0.5% acetic acid saturated H_2S (pH ~3) at 25°C for 3 days	Dodecyltrimethylammonium chloride - 98% inhibition	15
Steel SPY-3 L	5% NaCl + 0.5% acetic acid saturated H_2S (pH 3.0) at 25°C for 3 days	3 ppm of salt from reaction of oleylpyridine and butyl chloride gave 97% inhibition	16
Steel SPY-3 L	5% NaCl + 0.5% acetic acid saturated H_2S (pH 3) at 25°C for 3 days	20 ppm of polyamide by the reaction of lauric acid and triethylene tetramine gave 98% inhibition	17
Steel SPY-3 L	5% NaCl + 0.5% acetic acid saturated H_2S (pH 3) at 25°C for 3 days	20 ppm of quaternary imidazoline derivative gave 98% inhibition 	18
Steel SPY-3 L	5% NaCl + 0.5% acetic acid saturated H_2S (pH 3) at 25°C for 3 days	 $R^1 = C_{11}H_{23}$ R^2 - R^6 = H n = 3 20 ppm gave 98% inhibition	19

MATERIAL	MEDIUM	INHIBITOR	REFERENCE
Steel (?)	5% NaCl + 0.5 g acetic acid saturated H_2S	Best inhibitors - org nitrogen compounds with M.W >200. Substituted imidazolines with 9 carbons in hydrophobic chain and 2 aminoethylenes in the hydrophilic chain - best inhibition.	20
St. 3	Cl^-(1-9%); H_2S (500-2000 mg/L), 10-40°C, pH 3-7	Inhibitor IkIPG (500-1500 mg/L). Inhibition - 100%	21
Steel (?)	H_2S, oxygen (petroleum wells)	Heptyl, 2-5-ditert butyl-4 hydroxyphenyl phosphite (200 mg/L) 92% inhibition	22
St. 3, D and 12KhIMF	H_2S	Petroleum soluble aliphatic amines 200 mg/L - 97% inhibition	23
Steel (?)	H_2S, oxygen	 R = H or C_{1-4} alkyl; R^1 = H or Me or COOH Z = C_{1-4} alkylene; A = SO_3M, CO_2M, PO_3HM or PO_3M_2 M = H or cation; x -= o or 1	24
Steel st. 3	3% NaCl + 500 mg/L H_2S	Dialkyldimethyl ammonium chloride (C_{10}- 16 or C_{7-9}) alkyl groups	25
Steel D	Saturated H_2S	Amineacetylenic alcohols or esters; 1 g/L gave 83-97% inhibition	26
Steel rods	H_2S	Sulfoureide; 100-400 mg/L gave 100% inhibition	27
Steel (?)	Ethylamine containing H_2S and CO_2	10 g S/L forming polysulphides	28
Steel st. 3	3% NaCl - octane + 0.05% H_2S	1-2 mm/L   $BuS(CH_2)_2O(CH_2)_2O(CH_2)_2$-N  $C_7H_{15}SCH_2C(CH_3)HO(CH_2)_2O(CH_2)_2$-N 	29
Carbon steel	0.5 g NaCl/L + 1500-1700 mg/L H_2S at 20°C	Diethylenetriamine - N,N-dibutyronitrile; Diethylamino acetonitrile; Diallylamino acetonitrile; Piperidinobutyronitrile 0.005 to 1.0 g/L	30

MATERIAL	MEDIUM	INHIBITOR	REFERENCE
Steel st. 3	3% NaCl + 0.04% acetic acid saturated with H_2S	R:CO N(H):NH_2 Naphthenic acid hydrazide	31
Steel (?)	3% NaCl + 0.04% acetic acid in gasoline saturated with H_2S	Hydrazides, amides, N,-N dimethylaminopropyl or N-N diethylamino esters of naphthenic acids	32
Steel st. 3	1-5% NaCl + ≤2000 mg/L of H_2S + 0.4% HOAc with kerosine	IKG and IKIPG)aminoethyl derivative of comm alkyl phenol	33
Carbon steel	0.05% NaCl, pH 3.6 (acetic acid) saturated with H_2S	Diethylaminoacetonitrile; 0.05-1.0 g/L - 99% inhibition Family of compounds: $R_2(R_3)NR_1CN$	34
Carbon steel st. 3	H_2S	1-butyl-3(5)-methyl-4 nitro-pyrazole - 0.2 wt %	35
Steel D	Gas condensate H_2S 2.5-3 g/L	IS1 - 1,3-bis (ethanolaminomethyl)-imidazoline-2-thione IS2 - 1,3-bis (dibutylaminomethyl) imidazoline-2-thione IS3 - 1,3-bis(diethandaminomethyl) imidazoline-2-2-thione Inhibition efficiency >99%	36
Steel D	1:1 gas condensate-water saturated with H_2S	Distillate and dist residues from catalytic conversion of mono, di and tri-ethanolamines on a 10:90 Al-Cr catalyst - >99% inhibition	37
Mild steel	Monoethanolamine saturated with H_2S CO_2	1000 ppm of $CuCO_3$ and $KMnO_4$; Inhibition - 80%	38
Steel (?)	Aqueous ethanolamine CO_2, H_2S	Graft polymers - ethylene sulphide and polyethyleneimine in acetone/methanol/ /dioxane	39
Ferrous metal	H_2S	Aqueous solution of ammonium zinc carbonate, sulphide reduced from 1472 ppm to 4.0 ppm	40
Steel	Sour gas wells (H_2S, CO_2)	Removal of sulphur with ethylamine. Addition of elemental sulphur to regenerated ethylamine gave good inhibition.	41

MATERIAL	MEDIUM	INHIBITOR	REFERENCE
Steel st. 3	Saturated with H_2S	Disperse violet K; disperse pink Zh; disperse blue K; chrysodin, diphenylcarbazone hexamethylenediamine; Disperse blue K - 99% inhibition; hexamethylenediamine - 99% inhibition	42
Steel D	Gas condensate + water saturated with H_2S	Mixture of 2,3 and 2,4 dimethyl and 2,4,6 trimethyl pyridine (0.25-0.5 wt %) >95% inhibition	43
Steel	H_2S	By-product from synthesis of vitamins -VNIITB-1-dose - 0.045-2.0 kg/m^3	44
AISI 1010	80% monoethandamine saturated with H_2S	CuS and KMnO4 (1000 ppm each); oxidants such as $KMnO_4$, $Ca(MnO_4)_2$, potassium persulphate, KIO_3, $NaBrO_3$, $K_2Cr_2O_7$, O, H_2O_2, Na_2O_2, to produce S from H_2S	45
Steel st. 3	Benzene:water (1:1) + 0.04% acetic acid saturated H2S (750-800 mg/L)	R = Me, Et, Pr or Bu Z - 0, methylene or ethylene At 200-1000 mg/L - total protection	46
Steel (?)	80% CO_2 + 0.4% H_2S	Fatty acids	47
Mild steel	CO_2 + H_2S	500 ppm of reaction product of tetradecylbromide and alkyl pyridine + 50 ppm of NH_4SCN - 94% inhibition	48
Steel 3	H_2S	N,N dibutylnaphthamide, triphenyl phosphite, bis (alkyl phenyl) diethyl phosphoramidite	49
Steel st 3	H_2S	Reaction product of alkylsulphinates with carbamides, mixed dialkylcarbamides and sulpho derivatives of propionic acid	50
Steel 25	Gasoline sparged with H_2S	Inhibitor obtained by reaction naphthenic acids with diethylenetriamine and oleic acid - 10 mg/L gave 93% inhibition	51
Steel (?)	Sour gas conditioning solutions CO_2 + H_2S - 35% aqueous ethanolamine	500 ppm of alkyl pyridinium bromide + 500 ppm of HN_4SCN - inhibition was ~90%	52
Mild steel	30% aqueous ethanolamine saturated with CO_2	1-tetradecyl alkyl pyridinium salt (100 ppm) thioacetamide (25 ppm) + Co^{2+} acetate (50 ppm). inhibition - 95-96%	53

MATERIAL	MEDIUM	INHIBITOR	REFERENCE
Mild steel	30% aqueous ethanolamine saturated with CO_2 and 100-500 ppm of H_2S	Pentaethyleneamine + hexaethylene heptamine + quaternary salt - 90% inhibition	54
Steel 20, 40 Kh	H_2S saturated NaCl solutions of pH 6	Unsaturated derivatives of fluorine containing carboxylic acids	55
Steel st. 3	Acetic acid + H_2S	N,N_1 - dialkylethyl esters of cyclopentane carboxylic acid	56
Steel st. 3	Acetic acid H_2S + + benzene + NaCl	Dialkylamino alkyl esters of 3-cyclohexene carboxylic acid, 4-methyl-3-cyclohexene carboxylic acid	57
Steel (?)	H_2S - two phase emulsion system	Mixture of polymers and amines - nitrogen containing compounds gave synergism	58
Steel 45	Wastewater from oil field containing H_2S	I-1-V + H_3PO_4 or $Na_5P_3O_{10}$	59
Steel (?)	Gas condensate containing H_2S	Poly(vinyl amine) - M Wt 430-600	60
Steel st. 2	H_2S + HS + O_2 aqueous system	$Na_3PO_4.12H_2O$ and $Na_2O.3SiO_2$	61
Steel st. 3	Aqueous 0.5% NaCl + 250 mg/L acetic acid Petroleum condensate saturated with H_2S	Amines + quaternary ammonium salts C_{10-20} trimethyl alkyl ammonium chloride, C_{10-20} demethyl alkyl benzyl ammonium chloride, C_{17-20} dimethyl alkyl ammonium chloride = inhibition ~80-90%. Secondary amines were most effective	62
Steel	H_2S in aqueous drilling fluids	$CuCO_3$, $ZnCO_3$, $Zn(OH)_2$	63
Steel st. 3	Petroleum gas condensate and water saturated with H_2S	Mixture of inhibitors	64
Steel (?)	20% HCl, NaCl solution saturated with H_2S	Alkylbenzyl pyridinium chloride - 1% concentration	65
Mild steel	65% wt ethanolamine + CO_2	0.05% sodium metavanadte + 0.05% potassium antimonyl tartrate Inhibition ~99%	66

MATERIAL	MEDIUM	INHIBITOR	REFERENCE
Steel st. 3 and D	H_2S	Nitrogen bases, halo and alkoxymethyl substituted benzene derivatives - p-substitution gave better inhibition than o-substitution	67
Structural steel	High concentration of H_2S at 25°C and 45°C	Monoethanolamine	68
Steel [12597-69-2]	2-phase petroleum - aqueous NaCl + H_2S	HO R $C_6H_3CH_2NHCH_2CH_2NH_2$ obtained from alkylphenol, paraformaldehyde and ethylenediamine	69
Steel [12597-69-2]	Petroleum - 3% aqueous NaCl + H_2S	N-hydroxyalkyl amides	70
Structural steel	Two phase medium saturated with H_2S	Com. I-1-D - ANPO	71
Steel st. 3	Crude oil + 3% aqueous NaCl saturated with H_2S	Amides and their derivatives (obtained as condensation products of alkyl sukphonates with urea and mixtures of dialkyl urea and sulpho derivatives of propionic acid	72
Steel (?)	Acetic acid + HCl + NaCl + H_2S	Alkylbenzyl triethanolammonium chloride	73
Carbon steel	Gasoline with 0.1 N HCl Gasoline + 3% NaCl + saturated with H_2S Gasoline + 0.04% acetic acid + saturated with H_2S	$MePhO(CH_2)_3S$ CH_2NR_2(R = Me, Et, NR_2 = Morpholino) At 1000 mg/L inhibition was >92%	74
Steel (?)	H_2S	Neutralized product of sulpho acids with NH_2-CH_2-CH_2-OH and pyridine, sulphonated residue of pinene with NH_2-CH_2-CH_2-OH and quaternary ammonium salt from C_{14-15} aliphatic amine - 80-90% inhibition	75
SAE 1020	Brine - H_2S; Brine - CO_2	Monophosphonium compounds, $R_{2-3}P^+(CH_2\text{-}CH_2\text{-}CN)_{1-2}X^-$ polymeric phosphonium compounds - (R-alkyl, aryl) (.OQ.)$CH_2P^+R_3.X^-$ OQ-oxirane unit Superior to commercial inhibitors	76
Steel st. 3	3% NaCl-H2S at 20° and 40°C	IKIKhP-2 (condensation product of chloromethylated petroleum with pyridine)	77

MATERIAL	MEDIUM	INHIBITOR	REFERENCE
Steel (?)	0.01% SO_2, 0.01% H_2S 0.01% HCl	Triethanolamine oleate	78
Steel (?)	5% KCl saturated with H_2S	I-1-A (0.03%) - 94% inhibition ANPO (0.01%) - 96% inhibition Katapink (0.08%) - 90% inhibition	79
Steel [welding rod (SV-08A)]	H_2S in aqueous medium	Katapin A(alkylbenzyl pyridine hydrochloride); ANP-2 (a mixture of hydrochloride of aliphatic amines containing 15 carbon atoms)	80
Steel (SV08A)	Aqueous and aqueous hydrocarbon (Ugrain, Kerosine) containing H_2S, acetic acid (0.25 g) NaCl (5 g/L)	ANPO, Dodigen-E-1/214	81
Steel st. 3	Petroleum - NaCl containing H_2S	Dialkyldimethylammonium chloride	82
SAE-1020 steel	H_2S saturated synthetic sea-water	$NCH_2CH_2NHP(O)(OEt)_2$ $C_{18}H_{37}$ Imidazoline phosphoramide 4-16 ppm of $(Eto)2P(O)NH(CH_2CH_2NH)_2$ H.HCl gave 82% inhibition	83
Steel	Hydrocarbon-electrolyte (0.5% aqueous NaCl containing 250 mg/L of acetic acid saturated with H_2S	I-1-A (waste from 2-methyl-5-ethyl pyridine 400 mg/L gave 98% inhibition	84
Steel (?)	H_2S	$N^+R\ HSO_4^-$ (R - C_{10-12} group)	85
Steel (?)	H_2S	Rxn product of ß-hydroxybutyraldehyde with H_2S	86
Steel (?)	H_2S containing gas condensate	LPS-1 (lauryl pyridinium sulphate)	87
Steel (?)	Wet sour gas	0.001 wt % of a mixture of 1 mole of 2-ethylhexyl amine salt of phohoric acid monoester, diester and 6 moles of iso-propylamine	88
	Brine saturated with H_2S	Product from the rxn of pyridine with alkyl benzyl halides - 90% inhibition	89

MATERIAL	MEDIUM	INHIBITOR	REFERENCE
Steel (grade C7A)	3% aqueous NaCl saturated with H_2S, pH 1.0	Diamine dioleate (C_{10-16}) and katapinA gave 100% inhibition; Diamine dioleate from stearic acid, salt of monodiamine (C_{19}) and salicylic acid and salt of di-diamine C_{18} and salicylic acid gave >90% inhibiuon	90

REFERENCES (Appendix 2)

1. Z.G. Zulfugarov, P.S. Mamedova, I.F. Mamed'yarova, A.M. Kyazimov, R.A. Salamova, F.A. Abdullaeva and A.A. Turabova, Azerb. Khim. Zh., (5), 130 (1983); 101, 175541h (1984).

2. K. Oppenlaender, J. Stark and K. Barthold, Ger. Offen. DE 3,237,109, 12 April 1984; C.A. 101, 77145n (1984).

3. R.F. Miller, T.S. Go and G.R. Wilson, U.S. Patent 4,440,666, 3rd April 1984; C.A., 101, 27035f (1984).

4. A.M. Kuliev, T.D. Dzhafarova, F.N. Mamedov, F.A. Mamedov, R.K. Velieva and A.M. Kyazymov, USSR Patent 1,082,783, 30th March 1984; C.A., 101, 27036g (1984).

5. K. Oppenlaender, K. Stork and K. Barthold, Ger. Offen., DE, 3,232,921, 8th March 1984; C.A., 100, 212791S (1984).

6. V.S. Sagulenko, S.Sh. Dauenova, N.G. Kalacheva and E.M. Shvarts, USSR Patent, S.U. 967,053, 30th Aug. 1983; C.A., 99, 216875f (1983).

7. I.L. Rozenfeld, V.M. Brusnikina, L.N. Frolova, A.A. Lyashenko, Yu.V. Sokolov, B.V. Bocharov, A.N. Fokin, N.E. Legezin and E.V. Dergobuzova, U.S. Patent 4,404,167, 13th Sept. 1983; C.A., 99, 216876g (1983).

8a. K. Oppenlaender, K. Stork and K. Barthold, U.S. Patent 4,388,213, 14th June 1983; C.A., 99, 179937e (1983).

8b. K. Oppenlaender, K. Stork and K. Barthold, Ger. Offen., DE 3,119,376, 2nd Dec. 1982; C.A., 98, 147771j (1983).

9. E.C.Y. Nieh, U.S. Patent 4,372,873, 8th Feb. 1982; C.A. 98, 147780m (1983).

10. H. Tanji, H. Okazaki and M. Inoue, Aromatikkusu, 34, 275 (1982); C.A. 98, 130295j (1983).

11. Daido Steel Co., Japanese Patent, 57,164,928, 9th Oct. 1982; C.A. 98, 93841m (1983).

12. Kawasaki Steel Corp., Japanese Patent 57,149,424, 16th Sept. 1982; C.A., 98, 93842n (1983).

13. G.M. Ayubov and A.B. Abdullaeva, Azerb. Khim. Zh., (3), 77 (1982); C.A., 98, 76311w (1983).

14. I.L. Rozenfeld, V.M. Brusnikina, L.V. Frolova, A.A. Lyashenko, Yu.V. Sokolov, B.V. Bocharov, A.V. Fokin, N.E. Legezin and E.V. Dergobuzova, Canadian Patent, 1,114,594, 22nd Dec. 1091; C.A., 97, 59461g (1982).

15. Nippon Steel Corp., Japanese Patent, 81,90,986, 23rd July 1981; C.A., 96, 147319b (1982).

16. Nippon Steel Corp., Japanese Patent, 81,90,985, 23rd July 1981; C.A., 96, 147320v (1982).

17. Nippon Steel Corp., Japanese Patent, 81,90,984, 23rd July 1981; C.A., 96, 147321w (1982).

18. Nippon Steel Corp., Japanese Patent, 81,90,983, 23rd July 1981; C.A., 96, 147322x (1982).

19. Nippon Steel Corp., Japanese Patent, 81,90,982, 23rd July 1981; C.A., 96, 147323y (1982).

20. K. Suzuki, T. Kouno, E. Sato and T. Murata, Corrosion, 38, 384 (1982).

21. V.R. Vezinova, R.F. Sharifova, V.A. Spirina and G.G. Krimcheeva, Razrab. Mer Zashch. Met. Korroz. Mezhdunar, Nauchno-Tekh. Konf. Probl. SEV. 3rd, 5, 27 (1980); C.A., 95, 207636u (1981).

22. I.A. Mamedov, S.D. Zeinalov, D.S. Azaryaev, Yu.Yu.Yusupov, D.A. Aliev and O.K. Anakelova, Ibid., 5, 55 (1980); C.A., 95, 107637v (1981).

23. M.A. Mardanov, K.G. Veliev, L.M. Mir-Gashimova and R.S. Magerramov, Ibid., 5, 59 (1980); C.A., 95, 207638w (1981).

24. Ciba-Geigy Ltd. (Switz.), Res. Discl., 200, 529 (1980); C.A., 95, 84830t (1981).

25. Yu.Yu. Yusopov, I.A. Mamedov and V.N. Kozyrev, Fiz.-Khim. Mekh. Mater., 17, 36 (1981); C.A., 95, 47085h (1981).

26. A.N. Denisov and N.Yu. Babadzhanova, Gazov. Prom. St. Ser: Korroz. Zashch. Skvazhin, Trubo Provodov. Oberud. Morsk. Sooruzh. Gazov. Prom-Sti, (6), 13 (1980); C.A. 95, 19759e (1981).

27. I.A. Mamedov, A.M. Musaev and V.G. Yusifov, Azerb. Neft. Khoz., (2), 69 (1981); C.A., 94, 211181p (1981).

28. G. Schmitt and W. Bruckoff, Ann. Univ. Ferrara, Sez. 5 Suppl. 7 (1980) - (vol. 2, Eur. Symp. Corros. Inhibitors, 5th), 323 (1980); C.A., 94, 142240t (1981).

29. M.M. Movsum-Zade, F.N. Mamedov, N.R. Sultanova and N.V. Dzhafarova, Korroz. Zashch. Neftegazov. Prom-sti, (10) 8 (1980); C.A., 94, 92474z (1981).

30. I.L. Rozenfeld, V.M. Brusnikina, L.V. Frolova, A.A. Lyashenko, Yu.V. Sokolov, B.B. Bocharov, A.V. Fokin, N.E. Legezin and B.N. Altshuler, French Patent, 2,437,448, 25th April 1980; C.A., 94, 69726z(1981).

31. T.N. Dzhalilov, V.R. Vezinova, T.A. Gazinov, R.F. Sharifova and R.G. Gadzhieva, Gazov. Prom-sti, (6), 37 (1980); C.A., 93, 194226s (1980).

32. V.R. Vezirova, T.N. Dzhalilov, T.A. Gasanov, R.F. Sharifova and R.G. Gadzhieva, Korroz. Zashch. Neftegazov. Prom-sti, (6) 6 (1980); C.A., 93, 152737d (1980).

33. V.R. Vezirova, R.F. Sharifova, S.Yu. Pashaeva, A.M. Musaev, I.M. Ashrafov, R.G. Gaszhieva and N.K. Burzhueva, Gazov. Prom-st., (2), 35 (1980); C.A., 93, 134661v (1980).

34. I.L. Rozenfeld, V.M. Brusnikina, L.F. Frolova, A.A. Lyashchenko, Yu.V. Sokolov, B.V. Bocharov, A.V. Fokin, N.E. Legezin and E.V. Dergobuzova, Ger. Offen., 2,840,976, 27th March 1980; C.A., 93, 77475m (1980).

35. A.I. Bocharnikov, A.A. Sonochenko, V.Ya. Mudrakova, V.I. Seraya and V.A. Dubrovskaya, Zashch. Met., 15, 705 (1979); C.A., 92, 151076e (1980).

36. A. Kul'metov, Zh.G. Saidaliev, Zh.G. Safaev, A. Safaev and A. Kadyrov, Gazov. Prom-st., Ser: Korroz. Zashch Truboprovodov, Skvazhin, Gazopromysl. Gazopererab. Oborud., (4), 1 (1979); C.A., 92, 96493m (1980).

37. K.M. Akhmerov, A. Kul'metov, A.V. Kuchkarov and A. Akhmedov, Korroz. Zashch. Neftegazov. Prom-sti, (10), 12 (1979); C.A., 92, 96493m (1980).

38. R. Asperger, R.C. Clouse, B.D. Oakes and J.R. Davidson, Japanese Patent, 79,66,349, 28th May 1979; C.A., 91, 144338t (1979).

39. G.D. Jones and R.G. Asperger, J. Macromol. Sci. Chem., 13, 835 (1979).

40. V.R. Tisdale, U.S. Patent, 4,147,212, 3rd April 1979; C.A., 91, 96028t (1979).

41. W. Bruckoff, Endoel-Endgas-Z., 95, 82 (1979); C.A.91, 93975p (1979).

42. A.I. Bocharnikov, A.A. Sorochenkov and V.Ya. Mudrakova, Korroz. Zashch, Neftegazov. Prom-sti, (4), 11 (1979); C.A., 91, 77640v (1979).

43. K.M. Akhmerov, A. Kuchkarov, A. Ikramov and A. Kul'metov, Dokl. Akad. Nauk. U2bSSR (7), 56 (1978); C.A., 91, 76458e (1979).

44. R. Khasaev, L. Konysheva, L. Obukhova and V. Fedorenko, Neftyanik, (12), 11 (1978); C.A., 91, 76379e (1979).

45. R.G. Asperger, L.S. Krawczyk and B.D. Oakes, U.S. Patent 4,143,119, 6th March 1979; C.A., 90, 190718u (1979).

46. S.D. Zeinalov, S.B. Bilalov, M.M. Talybov and D.S. Azaryaev, Issled. Obl. Pererab. Miner. Resur. Azerb., 172 (1977); C.A. 90, 155390j (1979).

47. S. Hatala, A. Eczer, J. Takacs and J. Konc., Pr. Vyzk. Ustavu Geol. Inz., 35, 42 (1978); C.A., 90, 154391y (1979).

48. R.G. Asperger and R.C. Clouse, Ger. Offen., 2,814,126, 12th Oct. 1978; C.A., 90, 140895d (1979).

49. Z.G. Zul'fugarov, L.Sh. Zul'fugarova, R.K. Mamedova, A.M. Kyazimov, I.F. Mamed'yarova, R.K. Valieva, S.I. Gasanova and D.A. Akhundova, Issled. Obl. Pererab. Miner. Resur. Azerb., 29 (1977); C.A., 90, 197855t (1979).

50. I.A. Mamedov, N.M. Agaev, R.R. Mamedova, I.F. Mamed'yarova and R.K. Velieva, Ibid., 165 (1977); C.A., 90, 78310d (1979).

51. S. Wlodarczyk, M. Kajl, M. Wiekiera, E. Wilinska, H. Jodko and J. Tkaczyk, Polish Patent, 85,729, 30th Sept. 1976; C.A., 90, 57742f (1979).

52. R.G. Asperger, U.S. Patent, 4,102,804, 25th July 1978; C.A., 90, 27250b (1979).

53. R.C. Clouse and R.G. Asperger, U.S. Patent, 4,100,100, (1978); C.A., 89, 219162a (1978).

54. R.G. Asperger and R.C. Clouse, U.S. Patent 4,100,099, 11th July 1978; C.A., 89, 219163b (1978).

55. V.I. Starchak and L.M. Aparovich, Visn. L'viv. Politekh. Inst., 111, 16 (1977); C.A., 89, 63196b (1978).

56. T.N. Dzhalilov, T.A. Gasanov, R.K. Velieva and I.F. Mamed'yarova, Korroz. Zashch. Neftegazov. Prom-sti., (7), 9 (1977); C.A., 88, 29480j (1978).

57. T.N. Dzhalilov, T.A. Gasanov, R.K. Velieva and I.F. Mamed'yarova, ibid., (2), 10 (1977); C.A., 87, 155552b (1977).

58. R. Velieva, I.F. Mamed'yarova and A.M. Kyazimov, Mater. Dokl. Nauchn. Sess., Itogam. Nauchno-Issled. Rab. Resp. Koordiniruemym Akad. Nauk. Az. SSR Probl. Estestv. Obshchestv. Nauk, 1973, 11th, 9-11 (1974); C.A., 87, 139370k (1977).

59. A.P. Efremov, G.S. Orudzheva, A.G. Dorofeev, S.A. Grigor'ev and S.A. Asylkhanov, Korroz. Zashch Neftegazov. Prom-sti, (4), 17 (1977); C.A., 87, 42714n (1977).

60. K.M. Akhmerov, D. Yusupov and A.B. Kuchkarov, Uzb. Khim. Zh., (6), 67 (1976); C.A., 87, 25600e (1977).

61. S.N. Linevich and A.Ya. Naimanov, Izv.Sev.-Kavk. Nauchn. Tsentra Vyssh. Shk., Ser. Tekh. Nauk, 3, 103 (1975); C.A., 84, 8829g (1976).

62. T.V. Kemkhadze, Neft. Khoz, (2), 51 (1975); C.A., 84, 48413y (1976).

63. W.C. Browning and H.F. Young, U.S. Patent, 3,928, 211, 23rd Dec. 1975; C.A., 85, 96757f (1976).

64. A.D. Stepukhovich, N.V. Kozhevnikov and Yu.F. Myasnikov, Korroz. Zashch. Neftgazov. Prom-sti., (11), 6 (1975); C.A., 85, 97597r (1976).

65. F.N. Mamedov, F.A. Mamedov and M. Movsum-Zade, ibid., (3), 7 (1976); C.A., 85, 110653c (1976).

66. B.F. Mago and C.W. West, U.S. Patent, 3, 959,170, 25th May 1976; C.A., 85, 128587u (1976).

67. A.Z. Shikhmamedbekova, I.F. Mamed'yarova, S.A. Rasulova and R.K. Velieva, Korroz. Zashch. Neftegazov. Prom-sti, (12), 12 (1974); C.A., 83, 82346t (1975).

68. Z.P. Obukhova, A.A. Kutovaya and N.D. Manzon, ibid., (6), 3 (1972); C.A., 82, 33107m (1975).

69. E.D. Eilazov, I.S. Zamani and I.S. Sattar-Zade, ibid., (6), 6 (1972); C.A. 82, 33108n (1975).

70. I.A. Mamedov, N.M. Agaev, R.R. Mamedova and D.A. Akhundova, ibid., (12), 11 (1971); C.A., 82, 33102f (1975).

71. S.A. Ter-Karapetova, ibid., (12), 14 (1971); C.A., 82, 33103g (1975).

72. I.A. Mamedov, N.M. Agaev, R.R. Mirzoeva and D.A. Akhundova, ibid., (6), 3 (1974); C.A., 82, 20285t (1975).

73. A.G. Khanlarova, F.N. Mamedov, M.M. Movsum-Zade, V.R. Vezirova, R.K. Velieva and M.I. Shikhieva, ibid., (2), 7 (1974); C.A. 81, 138306h (1974).

74. Sh.I. Nazarov, S.D. Zeinalov, Sh.T. Akhmedov, Sh.z Omarov and M.L. Gasanova, ibid., (7), 13 (1973); C.A., 81, 84807r (1974).

75. E.D. Eilazov, I.S. Zamani and I.S. Sattar-Zade, Azerb. Neft. Khoz; 53, 44 (1973); C.A., 79, 138946a (1973).

76. D. Redmore, U.S. Patent, 3,664,807, 23rd May 1982; C.A., 77, 104 630m (1972).

77. I.A. Mamedov, N.M. Agaev, R.R. Mirzoeva and d.A. Akhundova, Issled. Ibl. Neorg. Fiz. Khim., 2, 242 (1971); C.A., 77, 91596c (1972).

78. A.I. Trufanova, E.Z. Bykhovskaya, L.P. Shirokova and V.N. Baibakova, Ingibitony Korroz., 121-8 (1970); C.A., 77, 91597d (1972).

79. T.V. Kemkhadze, I.A.Podol'nyi and V.V. Klepikov, Uch. Zap., Leningrad. Gos. Pedagog. Inst. in A.I. Gertsena, 433, 229 (1970); C.A., 77, 65232m (1972).

80. E.P. Sidorin, S.A. Balezin and I.V. Nikolskii, Uch. Zap., Mosk Gas. Pedagog. Inst. No. 340, 241 (1971); C.A., 77, 51533y (1972).

81. T.V. Kemkhadze, V.D. Fateev and E.P. Sidorin, ibid., No. 340, 254 (1971); C.A. 77, 51534z (1972).

82. I.A. Mamedov, N.M. Agaev, M.G. Rzaev, R.R. Mamedova and D.A. Akhundova, Izv. Vyssh. Ucheb. Zaved., Neft. Gaz., 15, 39 (1972); C.A., 77, 50955a (1972).

83. D. Redmore, U.S. Patent, 3,653,452, 4th April 1972; C.A., 77, 22586n (1972).

84. V.V. Klepikov, Gazov. Prom., 17, 13 (1972); C.A., 77, 22524r (1972).

85. N.E. Legezin, E.V. Dergobuzova and T.V. Kemkhadze, USSR Patent, 273, 979, 14th July 1970; C.A., 74, 78790e (1971).

86. W.D. Owsley, U.S. Patent, 3,585,069, 15th June 1971; C.A., 75, 78852x (1971).

87. S.F. Gudkov, T.V. Kemkhadze and V.V. Klepikov, Gazov. Prom., 16, 8 (1971); C.A., 75, 78804h (1971).

88. W.F. Anzilotti, U.S. Patent, 3,516, 922, 23rd June 1970; C.A., 73, 58565m (1970).

89. A.M. Kuliev, V.F. Negreev, R.K. Gadzhiev, F.N. Modemov, I.A. Mademov and R.S. Khalilov, C.A., 69, 108391s (1968).

90. V.F. Negreev, I.A. Mamedov and I.F. Madedov, Gazov. Delo, Nauch-Tekh Sb., (11), 15 (1966); C.A., 66, 69186h (1967.